DETERMINATION OF CHLORINATED DIBENZO-p-DIOXINS, CHLORINATED DIBENZOFURANS, CHLORINATED BIPHENYLS, CHLOROBENZENES AND CHLOROPHENOLS IN AIR EMISSIONS AND OTHER PROCESS STREAMS AT SWARU IN HAMILTON

(Part of Combustion Testing Program at SWARU in Hamilton)

Report No. ARB-02-84-ETRD

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Laboratory Services and Applied Research Branch Report

Acknowledgements

Our thanks are expressed to all sampling and laboratory personnel from Ontario Research Foundation and the Ministry of the Environment Dioxin and Pesticide Section laboratories who performed the work leading to the generation of data used in this report.

Special thanks are due to Dr. G. Van Volkenburgh for his gracious support and recognition of our efforts in bringing about this project to completion. Thanks are also due to Messrs. C. B. Martin and E. T. Barrow for their efforts in coordinating our activities with those of Envirocon Eastern Limited and Tricil Resources Inc.

Summary

Emissions of dioxins and furans measured in thirteen tests in the 1983 program were lower than the average emissions from the three tests performed in 1982. The variation in emissions between tests was somewhat larger this year, and the maximum and minimum emissions differed by a factor of 3.7 compared to 2.8 in 1982 (1,2). The highest emissions of dioxins and furans measured in one test in the 1983 program were comparable to the lowest emissions from the 1982 program. These emissions could result in point of impingement concentrations which are close to half hour criterion specifeid in the Provisional Air Guideline for dioxins and furans. However, the emissions measured in the remaining twelve tests in 1983 fall well below the guideline criterion. Similarly to 1982, dioxin and furan precursors - PCBs, chlorobenzenes and chlorophenols - were measured and found in the emissions, the refuse and the electrostatic precipitator ash. From among the three classes of precursors, PCB compounds were present at the lowest concentrations in all process samples, including the refuse. Dioxins and furans were found in small quantities in the refuse samples. Only trace quantities of all chlorinated species of interest were detected in the boiler bottom ash samples.

Introduction:

The work described in this report was a part of an experimental program with the purpose to examine the effect of operational variables on the emissions of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, henceforth called dioxins and furans, from one of the two smokestacks at the Solid Waste Reduction Unit (SWARU) facility in Hamilton. The background circumstances leading to the initiation of the sampling program, the emissions of species primary of interest - dioxins and furans - the emissions of PCBs, chlorophenols and chlorobenzenes, which all are chemical precursors preceeding the formation of dioxins and furans in combustion, and the emissions of particulate matter are outlined in this report. Besides the emissions, the concentrations of dioxins, furans and their precursors in the samples of municipal refuse fed to the boilers, of the flyash removed from the emissions by electrostatic precipitation and of the boiler bottom ash are also presented. Since emissions depend on process conditions, which in this program were purposely changed in each test, the results presented in this report reflect the effect of these changes and cannot necessarily be considered as representative of the normal everyday operation of the plant.

In addition to a short introductory part describing the background to program initiation and highlighting the main findings of the emission measurements, this report comprises two separate detailed reports on the sampling program and the subsequent chemical analyses of the emission samples. These reports were prepared by the sampling team from Ontario Research Foundation, and the Dioxin and Pesticide laboratories of the Ministry's Laboratory Services and Applied Research Branch respectively. Besides the measurements of chlorinated species in the emissions and other process streams, the emissions of other gaseous pollutants such as oxides of sulphur, carbon and nitrogen, and the concentrations of total hydrocarbons were determined by Envirocon Eastern Limited. Envirocon also monitored the process variables and combustion conditions during the tests. Their report contains all data including the results presented in this report, a detailed discussion of process conditions and a presentation on the correlation between the emissions of chlorinated aromatic compounds and process conditions.

Background

In late May and early June of 1982, the first measurements of dioxin and furan emissions were carried out at SWARU as a part of the Trace Organic Contaminants project. The measurements indicated that dioxin and furan emissions from SWARU may result in point of impingement concentrations which are higher than specified by the Ontario Point of Impingement Provisional Guideline for Chlorinated Dibenzodioxins and Dibenzofurans. Soon after this result became available, the rate of refuse firing at SWARU was decreased to meet the Provisional guideline annual ambient air concentration criterion for these compounds at the ground level. Also a new program was initiated, to examine the effects of process variables on dioxin and furan emissions and thus to provide a basis for the definition of operating conditions which minimize the air emissions of these compounds.

Some concerns about the accuracy of 1982 measurements and the interpretation of the analytical results, which have a direct bearing on the emission results, were expressed from both within and outside the Ministry. In order to answer these concerns, modifications to sampling and analytical protocols were made(3). The sampling time per test was decreased to four hours from 24 hours (used in 1982 testing) to facilitate an easier maintenance of steady process operation throughout each test. Another sampling train for precursors, in addition to the dioxin train, was specified, to obtain separate samples and to optimize the extraction procedures for the recovery of these compounds. The analytical protocol for dioxins and furans was simplified and a labelled 2,3,7,8-TCDD was specified as another spike, in addition to the labelled OCDD spike which was previously used alone for quality control of analyses. The rewritten sampling and analytical protocols were then sent to two analytical experts for review and comments. Their written comments (4,5), available from the Air Resources Branch upon request, were favourable; which was not surprising since the specified procedures are similar to those used by many sampling and analytical laboratories worldwide and the original protocol for the trace organic contaminants project already underwent reviews by various technical groups in the U.S. - E.P.A. in 1981. Some questions about sampling efficiency and the adequacy of the specified sampling trains still remained, but these were answered favourably in the course of work at SWARU, as discussed in the report by the Laboratory Services and Applied Research Branch. Recently obtained information from various E.P.A. sponsored studies in the U.S. also confirmed the adequacy of similar sampling procedures for dioxins, furans and their precursors (5).

The number of tests in the 1983 program at SWARU was determined by time and cost factors, which are outlined in more details in the Envirocon report. Here, it will suffice to mention that the magnitude of the level of measurement errors was of major importance. As for the scope of measurements, the knowledge of the emissions of precursors - PCBs, chlorobenzene and chlorophenols - in addition to dioxins and furans was considered essential for a complete emission analysis. The concentrations of dioxins ., furans and precursors in the feed, in the boiler bottom ash and the electrostatic precipitator ashes were also required for the proper interpretation of dioxin and furan emissions. The measurement of hydrogen chloride was omitted from the program since in previous tests the emissions of this compound varied little between the tests at the same incinerator, in contrast to dioxin and furan emissions which varied by a factor of more than 3.

Ontario Research Foundation, the Ministry's Dioxin and Pesticide Laboratories and the Air Resources Branch's Source Measurement Unit comprised the team responsible for the measurement of dioxins, furans and their precursors in the 1983 program. The same team was involved in the sampling of trace organic contaminants in 1982, including the program at SWARU, and therefore had the necessary experience and expertise in the emission measurements of trace chlorinated organics. The Source Measurement Unit and the Dioxin and Pesticide Laboratories of the Laboratory Services and Applied Research Branch were responsible for the development of the sampling and analytical protocols; Ontario Research Foundation was responsbile for field sampling, extraction of precursor samples and sampling report writing; the Laboratory Services and Applied Research Branch performed chemical analyses and prepared the laboratory report. The Source Measurement Unit was responsible for the coordination and management aspects of the program.

Results

The total emission concentrations and rates of the five groups of chlorinated species measured in the thirteen tests carried out on one of the two units at SWARU are shown in tables 22 and 27 on pages 66 and 71 respectively of the Ontario Research Foundation report. The emission rates of total dioxins and total furans ranged from 72.28 ug/s to 266.05 ug/s (micrograms per second). For comparison, the minimum and maximum emissions in 1982 at the same incinerator were 283 ug/s and 778 ug/s.

Dioxin and furan results were all corrected for internal standard or spike recoveries, as discussed on page 35 of the laboratory report. Error analysis and the accuracy of emission measurements are discussed in detail in both the Ontario Research Foundation report and the Laboratory Services and Applied Research Branch report under appropriate headings. Confidence ranges for emission rates are shown in table 41 on page 85 and the limits of 95% confidence range for each emission result in table 43 of the Ontario Research Foundation report. From this table, the maximum emissions of dioxins and furans measured in the 1983 program were 266 ± 76.3 ug/s.

The presence of precursors in the refuse and emissions from the SWARU boilers cannot be ignored in the analysis of dioxin and furans emissions. Precursors are less toxic compounds then dioxins, but they have been shown to react and form dioxins and furans under certain conditions in laboratory combustion experiments. Therefore, their presence in the refuse can be partially responsible for dioxin and furan emissions from SWARU.

Emissions in the 1983 program were measured when the process was operated in a manner which was not necessarily typical of normal everyday operation. However, they are also indicative of the fact that the SWARU facility can be operated in a manner which would limit dioxin and furan emissions such that the Provisional Guideline for Source Emissions is achieved.

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Trace Organic Contaminant Studies at SWARU. Part 1, Sampling.

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ORF

1. SUMMARY

A source sampling program was carried out to determine the concentrations and emission rates of specific trace organic contaminants from the Hamilton Solid Waste Reduction Unit (SWARU), Hamilton, Ontario. Contaminants of principal concern were polychlorinated dibenzo-p-dioxins (dioxins) and polychlorinated dibenzofurans (furans). Other contaminants of interest were chlorobenzenes, polychlorinated biphenyls (PCBs) and chlorophenols. The program was carried out only at the SWARU No. 1 boiler.

During a previous program, emission rates of dioxins and furans from the SWARU facility were relatively high and it appeared the Ontario Environmental Protection Act point of impingement provisional guideline for the combined dioxin and equivalent amount of furan maximum allowable impingement concentration of 450 pg/m^3 may be exceeded. The current program, sponsored by the Ontario Ministry of the Environment (MOE), was initiated to confirm the results of the previous study and to determine if the effects of SWARU plant operating conditions on the trace organic contaminant emission rates could be defined.

Ontario Research Foundation (ORF) was responsible for the source sampling program and a portion of the sample extraction program. The remainder of the sample extraction program and all sample analyses were carried out at the MOE Laboratories, Resources Road, Toronto. Another contractor, Envirocon Eastern Limited, was responsible for modifying the operating conditions, monitoring the operating conditions and correlating the operating conditions with trace organic contaminant emission rates.

This report, Part 1, details ORF's involvement in the study and includes calculated contaminant emission parameters based on analytical results received from the MOE Laboratory. Part 2 will detail the contribution of the MOE Laboratory to the study.

Thirteen emission tests were carried out using principally different conditions of refuse feed rate and combustion air to the SWARU No. 1 boiler unit. More tests were planned, but the program was shortened because of plant operating difficulties.

For each test, total concentrations and emission rates of each contaminant in the stack gases were determined as well as individual dioxin and furan congeners. Confidence ranges were derived for these emission parameters. Average parameters for the thirteen tests are summarised in the table below:

Contaminant	Concentration μg/m^3	Emission Rate μg/s
Dioxins	2.69 ± 0.76	44.4 ± 12.8
Furans	6.15 ± 1.29	102. ± 22.
Chlorobenzenes	42.5 ± 4.9	737 ± 93
PCBs	0.463 ± 0.036	7.91 ± 0.74
Chlorophenols	57.0 ± 4.6	979 ± 93

These average parameters are based on a number of plant operating conditions and do not necessarily reflect the emission parameters under typical plant operating conditions. The effects of specific operating conditions on the emission parameters will be addressed by Envirocon Eastern Limited.

Incremental samples of refuse, bottom ash and precipitator ash were collected simultaneously during each emission test. Composite samples were prepared at the conclusion of each test, extracted and analysed for the same trace organic contaminants.

Average results for the thirteen tests are summarised in the table below:

Contaminant	Concentration Refuse ng/g	 Bottom Ash ng/g	 Precipitator Ash ng/g
Dioxins	19.8	0.5	23.0
Furans	2.3	0.6	47.0
Chlorobenzenes	12.6	0.2	4.2
PCBs	79.8	0.4	1.4
Chlorophenols	521.3	3.0	43.0

Again, the above data were obtained for a number of plant operating conditions and do not necessarily reflect concentrations under typical plant operating conditions.

Emission sampling was carried out using EPA Method 5 sampling trains modified by the inclusion of two florisil traps in series between the third and fourth impingers. Two trains were operated simultaneously during each test which lasted four hours. Products collected from one train were eventually analysed for dioxins and furans whereas products from the other train were analysed for chlorobenzenes, PCBs and chlorophenols.

To improve and monitor the accuracy of the test data, special features incorporated into the emission study included proving all sampling equipment was clean, operating two trains simultaneously, using blank sampling trains, using duplicate florisil tubes, extracting train filters in two stages and using labelled dioxin spike solutions during sample extraction and analysis.

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2. INTRODUCTION

An emission assessment study carried out at the Solid Waste Reduction Unit (SWARU) in Hamilton, Ontario during 1982 indicated polychlorinated dibenzo-p-dioxins (dioxins) and polychlorinated dibenzofurans (furans) are emitted in the stack gases when municipal refuse is incinerated.

Dispersion calculations indicated ground level concentrations of combined dioxins and furans in the vicinity of the SWARU plant exceeded the current Ontario Ministry of the Environment (MOE) maximum permitted provisional guideline point of impingement concentrations for these compounds. These concentrations are 450 pg/m^3 for dioxins alone and 22,500 pg/m^3 for furans alone. These maximum concentrations are reduced if the dioxins and furans occur together, as is usually the case in combustion gases.

A second trace organic contaminant sampling program was initiated at SWARU, with the following objectives:

- confirm the results of the previous study using improved techniques for sample collection, extraction and analysis.
- determine if a decrease in the rate of garbage incineration and adjustment of the combustion air flowrate can be used to regulate the quantities of dioxins and furans released at SWARU, as either airborne emissions or in the incinerator ash.
- determine if the emission rate of dioxins and furans from SWARU, as either airborne emissions or in the incinerator ash, can be correlated with other incinerator operating parameters.

- determine if modifications to the electrostatic precipitators at SWARU have reduced airborne dioxin and furan emission rates.

- determine if quantities of dioxins and furans detected in the refuse and emissions at SWARU can be correlated with quantities of other trace organic contaminants, such as chlorophenols and polychlorinated biphenyls, which are recognised as precursors for dioxin and furan formation during incineration.

In the current study, Ontario Research Foundation (ORF) was requested to carry out the stack and process sampling program at SWARU. Another contractor, Envirocon Eastern Limited, was responsible for modifying and monitoring the incineration parameters during the source sampling program.

This report details ORF's contribution to the study.

3. PLANT AND PROCESS DESCRIPTION

The SWARU facility, operated by Tricil Limited, incinerates municipal refuse from the Hamilton area in two Babcock and Wilcox Canada Limited spreader-stoker boilers. Steam generated during incineration was to be marketed to neighbouring industrial plants, but, because of the severe fluctuations in supply, is now vented to the atmosphere. Emissions from each boiler pass through separate electrostatic precipitators and are emitted to the atmosphere through individual flues in a common stack.

Incineration is intended to be carried out twenty-four hours per day, five days per week.

Refuse is first dumped into a holding pit and then fed to four pulverisers using apron-type conveyors.

Shredded refuse from the pulverisers is passed on conveyors under magnetic separators to remove ferrous metallic scrap, and transferred to a holding bin. A conveyor moves the refuse from the bin to the boiler house where it is split into two streams to be fed to each of the two boilers. Three separate chutes feed the refuse to each boiler.

Fine material burns in suspension while the heavier material burns on the boiler stoker grate. The grate moves continuously towards the front of the boiler, and the speed can be adjusted to suit incineration conditions. Ash burnout time on the grate is about 60 s and the refuse incineration temperature can be as high as 1100°C. Overfired air and combustion air from below the grate are supplied for incineration. Generally, combustion of the refuse is self-sustaining although the boilers are equipped with natural gas burners should extraneous heating be required.

Boiler bottom ash is constantly discharged into a water quench hopper and eventually deposited on a pile in the plant yard. It is then trucked to a land fill site.

Hot gases generated in the combustion zone pass through the steam generation section and are reduced to about 310°C temperature. The cooled gases then pass through Wheelabrator electrostatic precipitators to remove particulate material. Flyash removed in the precipitators is collected in hoppers and water quenched. The wet flyash is stored on a similar pile to the boiler bottom ash and is eventually trucked to a landfill site.

After the precipitators, the flue gases are emitted to the atmosphere through a single stack which contains two individual flues, one for each incineration unit.

The capacity of each SWARU boiler is 272 tonnes refuse per day or 11.3 tonnes per hour, although the normal operating rate is usually about 9.0 tonnes per hour. The refuse contains about 10% moisture and has a heating value approximating 1.4×10^7 joules per kilogram.

A more detailed description of the plant and process, prepared by MOE personnel(1) is presented in Appendix 1.

4. SAMPLING STRATEGY

The entire sampling program was carried out only on the emissions from the SWARU No. 1 boiler unit.

Initially, it was intended that sixteen separate sampling tests would be carried out, but, because of frequent interruptions to the program through process malfunctions, only thirteen valid tests were completed, and one of these was terminated prematurely.

Each test included the collection of stack gas particulate and gaseous samples for subsequent trace organic contaminant analysis, and determination of trace organic contaminant concentrations and emission rates in the stack gases. Two sampling trains were used simultaneously. One, designated the dioxin train, was used to collect samples for dioxin and furan determinations and the other, designated the PCB train, was to collect samples for PCB, chlorophenol and chlorobenzene determinations. Blank sampling trains were also used at the sampling site to ensure that air entering the dioxin trains during leak checks was not contaminated with significant amounts of dioxins and furans.

Based on results from the previous trace organic contaminant sampling program at SWARU, the sampling time per test was selected to be four hours. In this sampling time, sufficient dioxins and furans should be collected so that, in subsequent analyses, quantities detected would be acceptably greater than the analytical detection limits.

Process samples, including raw refuse, bottom ash and precipitator flyash were collected about every hour during the stack sampling tests. It was expected at least six incremental samples would be obtained during each test because of additional time required for stack sampling, port changes and leak checks. At the end of each test, the incremental process samples were combined for trace organic contaminant extraction and analysis.

Prior to each stack sampling test, boiler conditions were established by Envirocon Eastern Limited. The conditions were then monitored by Envirocon, who were also responsible for the collection of all process data.

5. SAMPLING LOCATIONS

Trace organic contaminants in the No. 1 boiler emissions were collected by traversing the stack with sampling probes. The total stack height is 50.3 m and the sampling ports are located at the same level, 19.8m above ground and 10.7m above the top of the inlet breeching. The individual duct in the stack for No. 1 boiler emissions is elliptical with an equivalent diameter of 2.20m.

The sampling ports are in an ideal location with regard to the distance from the ports to the top of the stack, but non-ideal with regard to the distance from the breeching to the ports, which is about 5 stack diameters instead of the required 8 diameters.

If the ports were at entirely ideal locations, the total number of sampling points required during traverses of the duct with the sampling probe would be 20. To compensate for the non-ideality of the sampling locations, the number of sampling points was increased by at least 50%, and, in fact, 32 sampling points were used per test. Methods for determining the minimum number of sampling points is explained in the Ontario Ministry of the Environment Source Testing Code(2).

The major axis of the elliptical duct measured 2.90m, with ports at either end. Twenty-two sampling points were used on this axis, 11 through each port. The minor axis measured 1.68m with a single port. Ten sampling points were used on this axis. A single test, therefore, included material collected during traverses of both the major and minor axes of the duct through the three ports.

Since the total sampling time per test was 240 minutes, the sampling time per point was 7.5 minutes and sampling parameter readings were obtained every 2.5 minutes.

The duct cross-section is shown schematically in Figure 1.

Bottom ash samples were collected through three small inspection doors located side by side at the end of the moving grate. These samples could be obtained by opening the doors and inserting a shovel with a long handle to where the ash cascaded over the end of the grate into the water quench hopper.

The precipitator ash samples were collected from the hopper just below the rotary valve at the base of the electrostatic precipitator. A shovel was inserted through a door in the hopper and held beneath the valve but above the quench water at the bottom of the hopper during collection.

Refuse samples were collected by placing a shovel at the end of one conveyor belt in a series of conveyor belts which transfer the shredded refuse to the incinerator.

6. SAMPLING METHODOLOGY

The dioxin and PCB sampling trains were identical, modified EPA Method 5 trains. This modified train is shown schematically in Figure 2. A Method 5 train functions as follows:

A sample of stack gas is withdrawn isokinetically, via goose-neck nozzle and a heated probe (to prevent condensation) to a heated oven. The oven, usually maintained at about 121°C, contains a filter holder and glass fibre filter (sometimes preceded by a cyclone) to remove the particulate material. Following filtration, the sample passes through a series of four impingers immersed in an ice bath. Their purpose is to remove moisture by condensation. This permits the determination of stack gas moisture content and also protects downstream components from excess moisture. The first two impingers normally contain water (125 mL each). The third impinger is empty and the fourth contains silica gel. The stack gas, now filtered and dried, is drawn through an umbilical line (up to 30m long) to the control nodule.

Isokinetic sampling is maintained by relating the sampling rate, shown by an orifice meter, to the stack gas temperature and velocity. This mathematical relationship is established by a set of preliminary tests in which stack gas moisture, molecular weight and temperature are determined. Velocity is measured continuously with a pitot tube.

The modifications made to the Method 5 trains and procedures to enable trace organic contaminants in the stack gases to be sampled included:

- Two adsorbent traps containing florisil were placed in series between the third and fourth impingers to capture trace organic contaminants not retained by the train filter or impinger solutions. The second trap was used to detect breakthrough on the first trap.
- To minimise contamination, the sampling nozzles were nickel-plated and glass sampling probes were used. High purity deionised water, obtained from MOE laboratories, was used in the impingers.
- Because silicone grease and asbestos rope contain significant amounts of contaminants, Teflon seals were used throughout the sampling train.
- Extraordinary procedures, described in Section 7 of this report, were used to clean all sampling equipment and equipment used for sample recovery and extraction because dioxins and furans were expected to be present only in extremely small amounts. All the equipment likely to contact the samples was proven clean before use.
- Again, because of the low dioxin and furan concentrations, blank trains, prepared in the same way as the sample trains except only one florisil trap was used, were used to sample a quantity of the ambient air, equivalent in volume to the sampling train leak checks, in the vicinity of the stack to provide background trace organic contaminant concentrations.

7. EQUIPMENT CLEANING AND PROVING

To ensure that the very low concentrations of dioxins and furans expected to be present in the stack gases would be detectable, elaborate precautions were taken to clean the sampling train and sample extraction equipment before use.

Since previous experience has shown that, even after a thorough cleaning, some equipment is still contaminated with unacceptably high concentrations of trace organic contaminants, all of the equipment likely to contact the sampled stack gas was subjected to proving analysis before use. Proving analysis included rinsing the cleaned equipment with an organic solvent and collecting the rinsings for analysis.

Criteria were established for the maximum amount of contaminants which could be present in the rinsings before the equipment was unacceptable for sampling or extracting. To be acceptable, less than 100 ng polychlorinated biphenyls, including chlorinated aromatics, were to be present in the proving rinsings. Analyses were carried out by dual capilliary gas chromatograph/electron capture detector (GC/EC) techniques and, in addition to the groups of contaminants indicated above, proving rinsings were also unacceptable if other contaminants, such as phthalates, appeared in high concentrations at critical regions of the gas chromatogram.

The organic contaminants indicated above must be removed from the sampling equipment because, firstly, part of the program is designed to determine the emission rate of these contaminants and, secondly, some isomers of these contaminants have similar retention times to dioxins and furans during GC/MS analysis.

Equipment cleaning was accomplished using either rinsing, soaking or soxhlet extraction with one or more of a number of solvents including detergent, water, methanol, acetone, methylene chloride, hexane and pentane. Where applicable, the final proving extracts, which were either pentane or methylene chloride were reduced in volume to a few millilitres, an isooctane keeper added, and sent to the MOE Laboratories, Resources Road, Toronto, for analysis.

Individual cleaning procedures used for equipment and supplies are described in Appendix 2.

Results for the proving analyses made available to ORF, are presented in Appendix 3. Some results were not available for the following reasons:

- Some equipment was cleaned and proven for another trace organic contaminant study which was cancelled just before the SWARU study was initiated. This equipment was used for the SWARU study without further cleaning, but proving results are not available for this report, except that two of the proving analysis results were unacceptable and had to be recleaned. These samples are listed in Table 1.

- At the conclusion of each dioxin train test, the recovered products including the frit and intact florisil traps were sent to the MOE Laboratory, Resources Road, Toronto, for sample recovery and analysis. The frits and traps were recleaned and proven there before being returned to ORF for further use. Results are not available in this report for these analyses which are listed in Table 2.

- Some of the proving analyses, listed in Table 3, contained unacceptable levels of trace organic contaminants
In some cases the equipment was completely recleaned and reproven,
but in other areas, where contamination was slightly higher than the acceptable amount, only the final pentane rinse was repeated and it was not necessary to analyse this rinse before using the equipment for field work.

All proven equipment was sealed in cleaned and proven aluminum foil until use.

8. EQUIPMENT CALIBRATION

All the dry gas meters used for this study were calibrated at Ontario Research Foundation just before the field work commenced. A primary standard Warren and Collins chain-compensated gas meter, catalogue number 21013, was used.

The sampling probes to be used for the field work were completely assembled before calibration. This included insertion of the glass liners and attachment of new, freshly nickel-plated, 6.35 mm diameter nozzles. The nozzles were checked to ensure they had sharp tapers of less than 30° and that they had no nicks. Calipers were used to verify the dimensions of the inlet openings.

Assembled probes, numbers 5A, 5B, 5C, 5D and 5E, were calibrated at the Atmospheric Environment Services, Toronto, wind tunnel using procedures specified in the Source Testing Code(2).

Complete calibration data for the dry gas meters and sampling probes are presented in Appendix 4. Correction factors for each dry gas meter and sampling probe were 1.02 and 0.79 respectively.

Probe numbers 5F, 5G and 5H were received by ORF from the manufacturers just before the field work commenced, and although cleaned and proven, could not be calibrated before use in the field. These three probes were calibrated later, but for the purpose of calculating emission data, the pitot tube factors were assumed to be 0.79, and these factors were confirmed by the calibrations.

9. SAMPLING PROGRAM

Initially, sixteen separate stack sampling tests were planned for the No. 1 boiler flue gases using several different sets of combustion parameters.

The second and third tests were aborted shortly after commencing because of process malfunctions and, generally, succeeding tests were not completed as quickly as originally anticipated, also because of process malfunctions. Therefore, because of financial constraints, the final three tests in the study were cancelled indefinitely. Thirteen valid tests were completed, but in one of these, Test No. 14, only two stack traverses were completed instead of three.

The boiler parameters used for the thirteen valid emission tests are presented in Table 4. These parameters included the overfire air level and the quantity of steam generated by combustion heat.

A timetable for the stack emission tests is presented in Appendix 5. The dioxin and PCB trains were run simultaneously and actual sampling time was 4 h. However, because of time required for port changes, leak checks and process malfunctions, the elapsed time per test was much longer and was usually about 7 h per test.

While sampling was in progress, there were no sampling equipment malfunctions or sampling protocol variations which might significantly affect the test results. Similarly, sample recovery from the train proceeded without any serious problems. Some minor incidents during sampling and sample recovery are noted below.

During Test No. 7 there was an increase in the vacuum across the particulate filter of the PCB train to about 45 cm Hg during the third traverse, but this had only a minor effect on isokineticity. Plugging of the dioxin and PCB train filters occurred during the final 20 minute sampling for Test No. 8 and isokinetic sampling could not be maintained. This will have a minor effect on the overall test result since this period represents only 8.3% of the total sampling time.

Brownish stains were apparent on the train glassware during Test No. 10 and Test No. 12, but these stains were easily removed with acetone during sample recovery.

A few milligrams of particulate material was lost during filter recovery from the dioxin train for Test No. 6 and Test No. 8 and from the PCB train for Test No. 12. These losses were insignificant compared with the total amount of particulate material captured by the filters.

The process sampling timetable is also included in Appendix 5. Initially, it was intended that refuse, precipitator ash and bottom ash samples would be collected every hour during an emission test and then composited prior to extraction and analysis. Some samples were not collected on schedule for the following reasons:

- Equipment malfunction, such as breakdown of the refuse conveyor belt.

- It was undesirable to open the bottom ash doors during emission sampling since this would upset the combustion parameters.

Sufficient samples were collected during each test, however, that the final composites can be considered to be representative.

The emission sampling equipment used during each test is identified in Table 5, Table 6 and Table 7 for the dioxin trains, PCB trains and blank trains respectively. The equipment is identified by the proving sample number.

10. SAMPLE RECOVERY AND EXTRACTION

The extraction procedures used by ORF for the PCB sampling train components are presented in Appendix 6(3). After extraction, the samples were concentrated and sent to the MOE Laboratories, Resources Road, Toronto, for PCB, chlorobenzene and chlorophenol analysis.

At the conclusion of each field test, individual process samples were combined to form a test composite. The refuse samples were taken to the Centre for Resource Recovery, Toronto, for milling to less than 0.5 mm particle size. Milling procedures used in a previous trace organic contaminant study (Appendix 7) were used in the present study.

The bottom ash and precipitator ash samples were milled to less than 0.5 mm particle size in a thoroughly cleaned ceramic grinding mill at ORF.

After milling, the process samples were coned and quartered, and two representative portions collected for each sample. One portion was sent to the MOE laboratories, Resources Road, Toronto, for extraction and then analysis for dioxins and furans.

The remaining portions were extracted at ORF using the procedures described in Appendix 8(3). After extraction and concentration, the extracts were sent to the MOE Laboratories, Resources Road, Toronto, for chlorobenzene, PCB and chlorophenol analysis.

After sampling, the dioxin trains, PCB trains and blank trains were sealed with aluminum foil and returned to the ORF laboratory, where the samples were recovered.

The probe samples were recovered by three separate pentane washes which were collected in a single container. A brush was used to ensure recovery of particulate material. This process was then repeated using methylene chloride and these washings were retained in a separate container. Similar procedures were used to wash the nozzle and front half of the filter holder.

Each filter and frit was recovered and stored separately in petri dishes.

The impinger contents were transferred to suitable containers. Then the empty impingers, connecting glassware and rear half of the filter holder were rinsed several times, first with acetone and pentane, followed by methylene chloride. The methylene chloride wash was retained in a separate container.

Pairs of florisil traps from the dioxin trains and single traps from the blank trains were sealed with aluminum foil.

All of the above samples from the dioxin and blank trains were taken to the MOE Laboratory, Resources Road, Toronto, for extraction.

Prior to extraction of the process samples and train samples which were to be eventually analysed for dioxins and furans, quantities of labelled dioxin isomers in an iso-octane solution were added as a spike to monitor recoveries during extraction and analysis.

All spiking was carried out at the MOE Laboratories using ^{13}C labelled octachlorodibenzo-p-dioxin and ^{13}C labelled 2,3,7,8 - tetrachlorodibenzo-p-dioxin.

11. SAMPLE ANALYSIS

The analysis of all train and process samples for dioxins, furans, chlorobenzenes, PCB's and chlorophenols was carried out at the MOE Laboratories, Resources Road, Toronto.

Identification numbers of all samples prepared for analysis are presented in Appendix 9.

12. RESULTS AND DISCUSSION

12.1 Particulate Emission Rate

The quantity of particulate material collected by the main filter and probe rinse for the PCB trains are presented in Table 8. In the first two tests the probe rinse was filtered through the main particulate filter. However this procedure caused a slight weight loss for the main particulate filter, so, in succeeding tests, a separate filter was used for the probe rinse. In the dioxin trains the probe rinses were not filtered through the main particulate filter at the MOE Laboratories, Resources Road, Toronto, but through a separate probe rinse filter.

Particulate concentration and emission rate data for the dioxin and PCB trains are presented in Table 9. Generally, data for the dioxin and PCB trains are not in good agreement, perhaps for the following reasons:

- procedures for filtering the probe rinse differed for Test No. 1 and Test No. 2.
- the dioxin train probe rinse included pentane and methylene chloride, whereas the PCB train included only pentane.
- post-test filter weighings were carried out at the MOE laboratory (dioxin train) and ORF laboratory (PCB train) where conditions of temperature and relative humidity were unlikely to be identical. All pretest filter weighings were carried out at ORF.

Particulate concentration and emission rates, averaged for the thirteen tests, are presented in the table below:

Particulate Concentration

Train	Average Concentration mg/m^3	Concentration Range mg/m^3
Dioxin	148	27 - 400
PCB	268	47 - 675

Particulate Emission Rate

Train	Average Emission Rate g/s	Emission Rate Range g/s
Dioxin	2.50	0.38 - 6.95
PCB	4.67	0.79 - 11.05

Average sampling train filter oven temperatures for each test are also presented in Table 9. These temperatures were very similar for all tests, indicating the variations in particulate emission data between the dioxin and PCB trains were unlikely to have been caused by irregular condensation of volatile stack gas components on the main particulate filter from test to test through inconsistent filter oven temperatures.

Complete field data and computed results are presented in Appendix 10 for the dioxin tests and Appendix 11 for the PCB tests. Isokineticity data for the sampling periods are summarised in Table 10 for the dioxin tests and Table 11 for the PCB tests.

12.2 Stack Gas Physical Parameters

Stack gas physical parameters averaged during each dioxin test are summarised in Table 12 and similar data are presented in Table 13 for the PCB tests.

There is good agreement for the two series of tests, as indicated in the table below, of average results for the thirteen tests:

	Volume of Moisture %	Stack Gas Temperature °C	Dry Standard Flowrate m^3/s
Dioxin Tests	13.8	289.2	16.6
PCB Tests	13.4	294.6	16.9

12.3 Analyses of Stack Gas Samples

A report, prepared by the MOE Laboratories, Resources Road, Toronto, describing the analytical procedures and analytical results for the stack gas train samples and process samples, is presented in Part 2 of this study.

Extracts from the dioxin trains which were analysed individually are listed below:

- initial 16 h filter extract.
- second 16 h filter extract.
- impinger solution extract.
- first florisil trap extract.
- second florisil trap extract.

Similar extracts from the dioxin blank trains were analysed except that the second 16 h filter extract and the second florisil trap extract were not included. Only a single florisil trap was used with the blank trains.

During analysis, individual amounts of dioxin and furan congeners in the train sample extracts were obtained. These included tetra-, penta-, hexa-, hepta- and octa- congeners. The number of individual isomers observed for each congener in the extracts was also recorded.

Each congener analysis was corrected for spike recovery. Tetra-, penta- and hexa- congeners for both dioxin and furan were corrected using tetra-dioxin spike recovery, whereas the hepta - and octa - congeners were corrected using the octa-dioxin spike recovery. Correction was accomplished by dividing the initial analytical result by the appropriate spike recovery, expressed as a fraction. In some cases spike recoveries exceeded 100% because recoveries also reflect internal analytical equipment corrections.

Dioxin spike recoveries for each component of the dioxin sample trains are presented in Table 14. These recoveries ranged from 15% to 140% for the tetra-dioxin spike and from 4% to 150% for the octa-dioxin spike. Average overall recoveries were 62% for the tetra-dioxin spike and 43% for the octa-dioxin spike.

Average spike recoveries for each train component are indicated in the table below:

Train Component	Average Spike Recovery, % Tetra-Dioxin	Octa-Dioxin
Filter	54	39
Impingers	71	50
Florisil 1	56	31
Florisil 2	66	51
Average	62	43

The tetra-dioxin spike recovery is higher during sample extraction and analysis than the octa-dioxin spike.

Spike recoveries were not calculated for the second 16 h filter soxhlet extractions since none of the spiking material was detected.

The amounts of dioxin and furan congeners detected in the combined component extracts from each sampling train are presented in Table 15 and Table 16 respectively. Tetra-, penta-, and hexa-congeners generally predominate.

Distribution of these congeners throughout the sampling train components is indicated by data presented in Table 17. Average distributions are summarised in the table below:

Train Component	Contaminant Distribution, % Dioxins	Furans
Filter	50.9	49.1
Impingers	43.2	43.8
Florisil 1	4.9	5.6
Florisil 2	1.0	1.5
Average	100.0	100.0

Almost insignificant amount of dioxins and furans were collected by the florisil traps. In Test No. 10 and Test No. 11, however, for unknown reasons relatively large quantities of both dioxins and furans were detected in the second florisil trap extracts. Excluding these two tests, the amounts of dioxins and furans retained by the second florisil traps were only 0.2% and 0.3% respectively.

Relative amounts of dioxins and furans analysed for each emission test are given in the table below:

Test Number	Contaminant, % (Table 15 and Table 16)	
	Dioxins	Furans
1	22	78
4	41	59
5	24	76
6	32	68
7	25	75
8	25	75
9	22	78
10	34	66
11	21	79
12	35	65
13	19	81
14	47	53
15	40	60
Average	30	70

Or, the average ratio of furans to dioxins is 2.33:1.

Because of truncation, the total quantities of dioxins and furans detected for each test and presented in Table 15 and Table 16 are generally slightly different from the equivalent data presented in Table 17.

Total amounts of chlorobenzenes, PCB's and chlorophenols detected in the PCB train component samples are presented in Table 18. No additional data are available for individual isomers or for the distribution of these contaminants throughout the train components.

For chlorobenzenes and chlorophenols, only trichloro- and higher chlorine-substituted isomers were included in the analyses.

Altogether, 60 PCB isomers, ranging from dichloro- to hexachloro- substitutions, were included in the analyses.

12.4 Analysis of Process Samples

During extraction and analysis of the process samples for dioxins and furans, tetra-dioxin and octa-dioxin spikes were used in the same way as for treatment of the train samples. Spike recoveries for the process samples are presented in Table 19. These recoveries ranged from 1% to 330% for the tetra-dioxin spike and from 3% to 1000% for the octa-dioxin spike. Average overall spike recoveries were 95% for the tetra-dioxin spike and 116% for the octa-dioxin spike.

Average recoveries for each sample are indicated in the table below:

Process Sample	Average Spike Recovery, % Tetra-Dioxin	Octa-Dioxin
Refuse	17	23
Bottom Ash	128	70
Precipitator Ash	139	256
Average	95	116

These recoveries are much more variable than those encountered for the train samples. Duplicate analyses, however, indicated the high spike recovery values for the precipitator ash are reproducible.

Dioxin and furan analytical data for the process samples were reported by the MOE Laboratory as concentrations and these results are given in Section 12.6.

Chlorobenzene, PCB and chlorophenol analytical data were determined at the MOE Laboratory as the total amount of these contaminants in the process sample extracts received from ORF. The data are presented in Table 20. In Section 12.6 these analyses are presented as the equivalent concentration after correcting for the quantities of process sample used in each extraction. The same isomers were included in the process sample analyses as in the train sample analyses (Section 12.3).

12.5 Stack Gas Contaminant Emission Parameters

The concentration of each contaminant in the stack gas during each emission test was obtained by dividing the total quantity of contaminant detected in the sampling train by the volume of gas sampled at dry, standard conditions.

Quantities of contaminants collected are indicated in Table 15, Table 16, and Table 18. Volumes sampled are summarised in Table 21. The volumes from the dioxin train were used for dioxin and furan concentration computations, whereas the volumes from the PCB trains were used for chlorobenzene, PCB and chlorophenol concentration computations.

Total contaminant concentrations for each test are presented in Table 22. Average concentrations are indicated in the table below:

Contaminant Class	Average Concentration µg/m³	Concentration Relative to Dioxin
Dioxins	2.69	1.00
Furans	6.15	2.29
Chlorobenzenes	42.5	15.80
PCBs	0.463	0.17
Chlorophenols	57.0	21.19

Chlorobenzenes and chlorophenols were the major trace organic contaminants of the five classes detected in the stack gas emissions.

Dioxin and furan congener concentrations are presented in Table 23 and Table 24 respectively. These results are averaged in the table below:

Congener	Congener Concentration		Relative Concentration	
	Dioxin µg/m^3	Furan µg/m^3	Dioxin %	Furan %
Tetra-	0.76	2.56	28.3	41.6
Penta-	0.71	2.26	26.4	36.8
Hexa-	0.69	1.06	25.7	17.2
Hepta-	0.30	0.21	11.1	3.4
Octa-	0.23	0.06	8.5	1.0
Total	2.69	6.15	100.0	100.0

The dioxin and furan concentration data were derived only from analytical results for the stack sampling train and do not include subtraction of the amounts of dioxins and furans detected in the blank sampling trains. This approach is justified because, as shown in Table 25, blank train recoveries are insignificant compared with sample train recoveries. Generally the blank trains represent much less than 1% of the total dioxins or furans collected and the highest recovery was in Test No. 8 where furans detected in the blank train represented 2.41% of the furans detected in the sample train.

Stack gas contaminant emission rates were obtained as the product of the concentrations at dry, standard conditions (Table 22) and the dry standard stack gas flowrates presented in Table 26. The dioxin train flowrates were used for calculating dioxin and furan emission rates whereas PCB train flowrates were used for calculating chlorobenzene, PCB and chlorophenol emission rates.

Total contaminant emission rates are presented in Table 27 and average results are presented in the table below:

Contaminant Class	Emission Rate µg/s	Emission Rate Relative to Dioxin
Dioxin	44.44	1.0
Furan	101.92	2.3
Chlorobenzene	737.0	16.6
PCB	7.91	0.2
Chlorophenol	979.0	22.0

Emission rates for individual dioxin and furan congeners were derived from the concentration data (Table 23 and Table 24), and are presented in Table 28 and Table 29. Relative amounts of each congener series are indicated in the table below:

Congener	Emission Rates			
	Dioxins		Furans	
	µg/s	%	µg/s	%
Tetra-	12.82	28.8	42.83	42.1
Penta-	11.85	26.7	37.36	36.7
Hexa-	11.29	25.4	17.46	17.2
Hepta-	4.81	10.8	3.11	3.1
Octa-	3.69	8.3	0.89	0.9
Total	44.46	100.0	101.65	100.0

For dioxins, tetra-, penta- and hexa- predominate, whereas for furans tetra- and penta- congeners predominate. There are more furans than dioxins for tetra-, penta- and hexa- congeners, but more dioxins than furans for hepta- and octa- congeners.

12.6 Process Sample Contaminant Concentrations

Total contaminant concentrations in the refuse, bottom ash and precipitator ash are presented in Table 30, Table 31 and Table 32 respectively. Dioxin and furan concentrations were obtained directly from the MOE Laboratories, Resources Road, Toronto, where both sample extractions and analyses were carried out (Part 2 of this study). Concentrations of chlorobenzene, PCB and chlorophenol were calculated by dividing the analytical results obtained from the same MOE Laboratories (Table 20) by the initial amount of sample used by ORF for the sample extractions (50g).

The refuse concentrations, presented in Table 30, are all based on dry samples. There is a considerable range of concentrations from test to test for each contaminant class. Average concentrations and concentration ranges are summarised in the table below:

Contaminant Class	Average Concentration ng/g	Concentration Range ng/g
Dioxins	19.8	3.7 - 97.0
Furans	2.3	0.1 - 25.0
Chlorobenzenes	12.6	3.6 - 44.0
PCBs	79.8	6.4 - 800.0
Chlorophenols	521.3	1.0 - 2000.0

Average bottom ash contaminant concentrations, derived from the results presented in Table 31, are summarised in the table below:

Contaminant Class	Average Concentration n/g	Concentration Range n/g
Dioxins	0.5	0.1 - 3.3
Furans	0.6	0.1 - 3.9
Chlorobenzenes	0.2	0.1 - 1.1
PCBs	0.4	0.1 - 2.0
Chlorophenols	3.0	0.1 - 10.0

These concentrations are all obviously much lower than equivalent concentrations for the refuse samples.

Similar average results for the precipitator ash samples, derived from Table 32, are summarised in the table below:

Contaminant Class	Average Concentration ng/g	Concentration Range ng/g
Dioxins	23.0	6.2 - 94.2
Furans	47.0	22.0 - 105.0
Chlorobenzenes	4.2	1.0 - 20.0
PCBs	1.4	0.1 - 4.0
Chlorophenols	43.0	0.1 - 240.0

These concentrations are much higher than equivalent concentrations for the bottom ash samples and, for dioxins and furans only, are higher than equivalent refuse concentrations. Quantities of both bottom ash and precipitator ash produced, however, would both be much less than the quantity of refuse consumed by the incinerator.

Individual dioxin and furan congener concentrations for the refuse, bottom ash and precipitator ash process samples are presented in Table 33, Table 34 and Table 35 respectively.

For the refuse samples (Table 33) the octa-congener predominated with lesser amounts of the hepta-congener. The tetra-, penta- and hexa- dioxin congeners were generally not detectable. Most of the furan congeners were not detected. Those which were detected were present in small quantities.

None of the dioxin or furan congeners predominated in the small amounts of these contaminants detected during analysis of the bottom ash samples (Table 34).

The tetra-, penta- and hexa- congeners predominated in the precipitator ash samples (Table 35), as the average results in the table below indicate:

Congener	Precipitator Ash Concentration			
	Dioxins		Furans	
	ng/g	%	ng/g	%
Tetra-	3.7	16	11.8	25
Penta-	6.4	28	17.2	37
Hexa-	9.1	40	14.3	31
Hepta-	2.3	10	2.8	6
Octa-	1.5	6	0.3	1
	23.0	100	46.4	100

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13. ACCURACY OF EMISSION PARAMETERS

13.1 General

A number of quality control procedures were incorporated into the SWARU trace organic contaminant program to ensure that the emission data were as accurate as possible.

These procedures were necessary because dioxins and furans, the trace organic contaminants of principal interest in this study, are usually present in emission sources at extremely low concentrations (ppt to ppb range) and, secondly, methods for trace organic contaminant sampling and analysis are relatively new and have not been extensively evaluated.

Descriptions of these procedures were provided in earlier sections of this report. In the remainder of this section their contribution to improving the accuracy of the emission data is summarised. The actual accuracy cannot be calculated, however, since the true contaminant emission rates are not known.

13.2 Cleanliness of Sampling Equipment

Because of the low concentrations of some trace organic contaminants expected to be present in the SWARU emissions, all equipment likely to be in contact with the emission samples during sampling, extracting and analysing was thoroughly cleaned and proven clean. Cleaning procedures were described in Section 7 and Appendix 2. No equipment was used until it was shown to be acceptably clean. The criteria used for determining cleanliness were based on reducing to a minimum the presence of organic compounds which were to be detected during the sampling program (dioxins, furans, chlorobenzenes, PCBs and chlorophenols) and other organic compounds which might cause interference during analysis by GC/MS techniques.

In addition to thoroughly cleaning all equipment, only high purity reagents were used throughout the sampling, extracting and analysing procedures. These reagents included distilled-in-glass grade solvents, deionised water, cleaned and proven florisil, and high purity hydrochloric acid.

13.3 Sampling Train Efficiency

The trace organic contaminant sampling trains each had a number of components in series to capture contaminants in the sampled gas stream. These components, in order of contact with the gas stream, included a particulate filter, two impingers containing water and two florisil traps. Two florisil traps were used so that any breakthrough into the second trap could be observed.

It was shown in Section 12.3 that, for example, only 1.0% of the dioxins and 1.5% of the furans captured on average by the dioxin trains were recovered from the second florisil trap, the last component of the sampling train. It can be concluded from these data that the dioxin trains were essentially capturing all dioxins and furans in the sampled stream; otherwise contaminants retained on the second trap would be higher.

13.4 Sampling Reliability

Determination of emission parameters requires accurate measurement of the quantity of stack gas sampled and the stack gas flowrate, both at standard conditions. Procedures normally used in source sampling to improve the accuracy of these measurements includes calibration of the dry gas meter, sampling probes, thermocouples and gravimetric balances. Isokineticity calculations are used to validate sampling rates.

An additional feature used in the current study to improve sampling reliability included operating the dioxin and PCB trains independently, but simultaneously. Data obtained from the two trains during a single test for physical stack gas parameters such as moisture content, temperature and flowrate should be comparable.

These data, presented in Table 12 and Table 13, indicate similar results from the two trains in a single test. The average percentage of isokineticity data, presented in Table 10 and Table 11, are all within the acceptable range of 90% to 110% of isokineticity.

The emission data obtained from each train can also be used to calculate the precision of the sampling procedures and develop confidence ranges for the emission parameters. This subject is discussed in Section 14 of this report.

13.5 Sample Contamination

Blank trains were used during each test to monitor contamination by organic compounds during sampling, extracting and analysing. These blank trains were initially cleaned, assembled and then taken to the sampling site along with the sampling trains.

The quantity of ambient air in the vicinity of the stack which was drawn into the sampling trains during leack checks was also drawn into the blank trains. These trains were then dismantled and the components treated analogously to the sample train, including extraction and analytical procedures.

As indicated in Section 12.5 and Table 25, the quantities of dioxins or furans detected in the blank trains were never more than 2.41% of the amount detected in the sample trains. It can be concluded, therefore, that since sample contamination did not occur during leak checks, sample recovery, extraction or analysis for the thirteen blank train tests, it did not occur during similar operations for the dioxin and PCB trains.

13.6 Extraction Efficiency

Extraction of trace organic contaminants from the sampling train components included established procedures such as soxhlet extractions, liquid - liquid extractions, elutions and ultrasonic extractions. It was expected that soxhlet extraction of the sampling train filters would be the most difficult procedure for attaining high contaminant recoveries. Therefore, to assess recovery, two successive extractions were carried out on each dioxin train filter. Each extraction was of 16 h duration and the extracts were analysed separately.

Results for these analyses are presented in the table below:

Test Number	First Extract		Second Extract	
	Dioxins ng	Furans ng	Dioxins ng	Furans ng
1	2750	7820	42	44
4	772	762	ND	ND
5	2210	4935	44	82
6	8610	11,815	155	247
7	3640	8480	30	37
8	1030	2331	3	11
9	2880	9391	3	14
10	721	899	5	6
11	1710	6019	90	406
12	555	584	1	3
13	1750	7000	ND	3
14	4220	5238	72	96
15	943	916	4	3
Average	2445	5630	35	73

ND = None Detected

Only 1.4% of the dioxins and 1.3% of the furans recovered during soxhlet extraction were recovered during the second 16 h extraction. It can be concluded that essentially all the dioxins and furans recoverable from the particulate filters were recovered during the soxhlet extractions. This does not preclude the fact, however, that not all dioxins and furans associated with the stack gas particulate material may be extractable.

13.7 Analytical Efficiency

Each sample recovered from the dioxin trains was spiked with a labelled mixture of dioxin isomers before extraction and analysis.

Spiking was carried out at the MOE Laboratories, Resources Road, Toronto, and was used mainly for adjusting dioxin and furan analyses to reflect analytical instrument operating parameters. Since the spiking mixtures were added to the samples immediately after recovery from the sampling trains, the final spike recoveries also compensated for loss of dioxin and furan compounds during extraction and clean-up of the sample extracts. It was assumed that behaviour of the spiking isomers during extraction and analysis was analogous to similar material originating from the stack gases. This point is discussed more fully in Part 2 of this study.

14. PRECISION OF EMISSION PARAMETERS

14.1 General

The trace organic contaminant stack gas emission parameters presented in Table 22 and Table 27 as total concentrations and emission rates, respectively, were not accompanied by any indication of accuracy or precision.

Accuracy is important because it is a measure of the difference between the experimentally determined emission parameters and the actual emission parameters.

Unfortunately, as mentioned earlier, the actual emission parameters are not known and the accuracy cannot be calculated. A number of measures, however, were incorporated into the dioxin and furan sampling, extracting and analysing phases of the program to either improve or monitor the accuracy of the emission parameters. These measures were explained in Section 13 and included the use of two florisil traps, dual trains, double extractions of particulate filters, proving of sampling equipment and the use of spikes during sample extraction and analysis to improve experimental accuracy. Accuracy was monitored by separately analysing the two florisil traps and filter extracts, and by operating blank sampling trains to provide background concentrations of dioxins and furans.

Since the analyses of the second florisil trap, second filter extracts and blank sampling train components indicated insignificant amounts of dioxins and furans, it can be concluded the experimental emission parameters are reliable.

Precision is a measure of expected variability in experimental data and it is important because it enables confidence ranges to be calculated for the emission parameters. To calculate precision, replicate data are required. This is available in the present study, to some extent, because the dioxin and PCB trains were run simultaneously during each test and the trains were essentially identical. Also duplicate analyses for dioxins and furans were carried out on some of the sample extracts.

In the remainder of this section, calculations related to determining precision are presented. It should be noted that the replicate information available provide an estimate of the overall error. However, these data are limited and do not include all factors.

To calculate confidence intervals for the trace organic contaminant concentrations and emission rates, individual precisions for the stack gas volume sampled, stack gas flowrate and sample analyses must be determined since these parameters are linked by the following equations:

$$(a)\quad \text{Concentration} = \frac{\text{Sample Analysis}}{\text{Volume Sampled*}}$$

$$(b)\quad \text{Emission Rate} = \frac{\text{Sample Analysis x Flowrate*}}{\text{Volume Sampled*}}$$

(* At dry reference conditions)

14.2 Differences Between the Sampling Train Data

The volume of stack gas sampled and stack gas flowrate data for the dioxin and PCB trains are presented in Table 21 and Table 25 respectively. Before the data from the two trains can be regarded as duplicates for the purposes of calculating sampling precision, it is necessary to determine if there is a significant difference between the two trains.

An examination of the data shows that in 5 of the 13 tests, the volume sampled was higher with the dioxin train than with the PCB train and in 3 of the 13 tests the calculated flowrate was higher with the dioxin train than with the PCB train. Therefore there does not appear to be a dominant systematic bias or one train would consistently give higher results than the other.

There will, of course, be many minor differences in the two sampling trains which will bias volume sampled and flowrate determinations. It is impossible to determine the individual effects of these differences in this study, but this is not critical since only their combined effect on the volume sampled and flowrate is important during a comparison of data from the two trains.

Apart from considering which train gives the highest volume sampled and flowrate values during each test, a statistical method was used to determine if the trains were significantly different. The Student t test(4) was used and details are provided in Table 36. At a 95% confidence level there was no significant difference between the volume sampled data for the two trains [t(calculated) = 1.71 which is less than t(95%) = 2.18]. There was a significant difference between flowrates at a 95% confidence level, but not at a 98% confidence level [t(calculated) = 2.43 which is less than t(98%) = 2.68]. Overall, however, the trains were regarded as duplicates, permitting the volume sampled and flowrate data to be used for calculating test precision, although it is recognised that the differences in data obtained from the two trains may also be due to process variables such as stack gas stratification in addition to slight variations in sampling equipment and techniques.

14.3 Confidence Range for Volume Sampled, Flowrate and Analyses

A preliminary step in the calculation of confidence ranges is to estimate the standard deviation. For paired data, the standard deviation can be estimated from the formula(4):

$$\text{(c)} \quad \sigma = \frac{\Pi^{1/2}\ (a-b)}{2n}$$

where:
σ = Estimated standard deviation
a,b = Individual values of paired data
n = Number of duplicate data
Π = Pi

In this case, a and b can be volume sampled, flowrate or an analytical result obtained from the dioxin train and PCB train in a single test.

Once the estimated standard deviation is known, confidence ranges can be calculated from the following formula:

(d) $\mu = x \pm Z\sigma$

Where: μ = "True" parameter value
x = Experimental parameter value
Z = Standard deviate

At a 95% confidence level, the value of the standard deviate is 1.960. The product $Z\sigma$ is a measure of the precision of the experimental parameter, in this case volume sampled, flowrate or an analytical result.

The confidence ranges are presented in Table 37, Table 38 and Table 39 for volume sampled, flowrate and dioxin plus furan analyses respectively.

Confidence ranges for the dioxin and furan analyses were based on duplicate analyses only for three impinger solutions and do not include the effects of sample extraction or extract clean-up. These latter effects, however, are compensated by correcting the analytical data for spike recovery and do not have to be included in confidence range calculations.

These confidence ranges were all based on the formula:

(e) $\mu = x \pm \frac{1.737\ \Sigma\ (a-b)}{n}$

Confidence ranges for the chlorobenzene, PCB and chlorophenol analyses are presented in Table 40. Since the MOE Laboratory, Resources Road, Toronto, provided standard deviations for replicates of these analyses, which also included sample extraction and clean-up, the following alternative formula was used for calculating the confidence intervals:

(f) $\mu = x \pm 1.960\ \sigma$

Based on average results, confidence ranges are summarised in the table below:

Parameter	Average Result	Absolute Confidence Range	Percentage Confidence Range
Volume Sampled	$1.92/m^3$	$\pm$ 0.149 m^3	$\pm$ 7.76%
Flowrate	16.77 m^3/s	$\pm$ 0.87 m^3/s	$\pm$ 5.19%
Dioxin Analysis	549 ng	$\pm$ 149 ng	$\pm$ 27.14%
Furan Analysis	2618 ng	$\pm$ 509 ng	$\pm$ 19.44%
Chlorobenzene Analysis	100 ng	$\pm$ 8.49 ng	$\pm$ 8.49%
PCB Analysis	3000 ng	$\pm$ 7.45 ng	$\pm$ 0.25%
Chlorophenol Analysis	833 ng	$\pm$ 16.95 ng	$\pm$ 2.03%

These confidence ranges can now be used to calculate equivalent ranges for the trace organic contaminant concentrations and emission rates. Because the absolute confidence range is likely to be directly proportional to the magnitude of the measured parameter, the percentage confidence range results should be used to calculate the confidence range for individual tests. This is equivalent to stating that the absolute confidence range is not independent of the magnitude of the measured parameter.

14.4 Confidence Range for Emission Parameters

The confidence range for the trace organic contaminant concentration in the stack gases can now be calculated from the following formulae$^{(5)}$:

$$\text{(g)} \quad \text{Concentration} = \frac{\text{Analysis}}{\text{Volume}}$$

$$\text{(h)} \quad \underset{(\text{Concentration})}{\%\text{C.R.}^2} = \underset{(\text{Volume})}{\%\text{C.R.}^2} + \underset{(\text{Analysis})}{\%\text{C.R.}^2}$$

Where: Concentration = Contaminant concentration
Volume = Volume of stack gas sampled
Analysis = Contaminant analysis in sample
% C.R. = Percentage confidence range

Similarly, the confidence range for the trace organic contaminant emission rate can be calculated from these formulae:

$$\text{(i)} \quad \text{Emission} = \text{Concentration} \times \text{Flowrate}$$

$$\text{(j)} \quad \underset{(\text{Emission})}{\%\text{C.R.}^2} = \underset{(\text{Concentration})}{\%\text{C.R.}^2} + \underset{(\text{Flowrate})}{\%\text{C.R.}^2}$$

Where: Emission = Contaminant emission rate
Flowrate = Stack gas flowrate

Confidence ranges for concentrations and emission rates for the five contaminant classes are presented in Table 41. From these confidence ranges average concentrations and emission rates for the 13 tests are presented in the table below:

Contaminant	Concentration g/m^3	Emission Rate g/s
Dioxins	2.69 ± 0.76	44.4 ± 12.8
Furans	6.15 ± 1.29	102 ± 22
Chlorobenzenes	42.5 ± 4.9	737 ± 93
PCBs	0.463 ± 0.036	7.91 ± 0.74
Chlorophenols	57.0 ± 4.6	979 ± 93

These average data may not necessarily represent the emission parameters for typical SWARU operating conditions since they were obtained from a number of different operating conditions.

Absolute confidence ranges for individual tests, obtained by determining the product of the emission parameter (concentration or emission rate) and the appropriate percentage confidence range, are presented in Table 42 and Table 43.

14.5 Percentage Deviation

Another useful measure of precision in addition to confidence ranges is the percentage deviation of individual experimental data from the mean of duplicate data. Percentage deviation is calculated by subtracting individual data from the duplicate data mean, converting to a percentage and then averaging these percentages for all the available data.

These calculations were applied to the 13 duplicate results from the dioxin train and PCB train for volume sampled and flowrate and to the 3 duplicate results from the dioxin and furan analyses of three impinger solutions.

The results are summarised in the table below:

Parameter	Average Deviation
Volume Sampled	2.20%
Flowrate	1.48%
Dioxin Analysis	6.73%
Furan Analysis	5.30%

These results are an indication of how effectively experimental data can be duplicated. Obviously volume sampled and flowrate can be duplicated extremely well with dioxin analyses and furan analyses being duplicated somewhat less easily.

The analytical data do not include the effects of sample extraction or clean-up of the extract before analysis.

Similar duplicate data are not available for the chlorobenzene, PCB and chlorophenol analyses.

REFERENCES

(1) Process Description of Hamilton Solid Waste Reduction Units (SWARU) Waste to Energy Recovery Incineration Facilities, G. Wong, March 10, 1983.

(2) Ontario Ministry of the Environment Source Testing Code, Report No. ARB-TDA-66-80, November 1980.

(3) Stack Sampling for Trace Organic Contaminants, Schedule No. 2, Version No. 5 - SWARU.

(4) Applied Statistics for Engineers, 2nd Edition, W. Volk, McGraw Hill, 1969.

(5) Industrial Source Sampling, D. Brenchley, C.D. Turley, R.F. Yartnac, Ann Arbour Science, 1973.

TABLE 1

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
SAMPLING EQUIPMENT CLEANED PRIOR TO THE SWARU STUDY

Sample Number	Sample Description
S1	Blank Train No. 1
S2	Blank Train No. 2
S3	Blank Train No. 3
S4	Blank Train No. 4
S5	Blank Florisil Trap No. 1
S6	Blank Florisil Trap No. 2
S7	Blank Florisil Trap No. 3
S8	Blank Florisil Trap No. 4
S9	Glass Wool, Pentane
S10*	Glass Fibre Filters, Pentane
S11	Glass Wool, Dichloromethane
S12	Glass Fibre Filters, Dichloromethane
S13	Test Train No. 1
S14	Test Train No. 2
S15*	Test Train No. 3
S16	Test Train No. 4
S17	Florisil Trap No. 1
S18	Florisil Trap No. 2
S19	Florisil Trap No. 3
S20	Florisil Trap No. 4
S21	Florisil Trap No. 5
S22	Florisil Trap No. 6
S23	Florisil Trap No. 7
S24	Florisil Trap No. 8

* Sample Required Recleaning.

TABLE 2

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

MOE DIOXIN LABORATORY EQUIPMENT CLEANING AND PROVING

Sample Number	Sample Description
S131	Florisil Trap No. 31
S132	Florisil Trap No. 32
S160	Florisil Trap No. 36
S161	Florisil Trap No. 37
S162	Florisil Trap No. 38
S163	Florisil Trap No. 39
S177	Florisil Trap No. 42
S178	Florisil Trap No. 43
S189	Florisil Trap No. 44
S190	Florisil Trap No. 45
S218	Florisil Trap No. 53
S219	Florisil Trap No. 54
S220	Florisil Trap No. 55
S221	Florisil Trap No. 56
S245	Frit No. 13
S246	Frit No. 14
S247	Frit No. 15
S248	Frit No. 16
S249	Frit No. 17
S261	Florisil Trap No. 63
S262	Florisil Trap No. 64
S263	Florisil Trap No. 65
S264	Florisil Trap No. 66

ORF

TABLE 3

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

SAMPLING EQUIPMENT REQUIRING RECLEANING

Initial Sample Number	Sample Description	Type of Recleaning	
S10	Glass Fibre Filters, Pentane	Recleaned, Reproven	(S29,S30)
S15	Test Train No.3	Recleaned, Reproven	(S28)
S59	Glass Wool, Dichloromethane	Recleaned, Reproven	(S103)
S60	Blank Train, No. 6	Recleaned, Reproven	(S89)
S61	Blank Train, No. 5	Recleaned, Reproven	(S90)
S66	Blank Train, No. 7	Recleaned, Reproven	(S147)
S69	Test Probe No. 5A	Recleaned, Reproven	(S87)
S70	Test Probe No. 5C	Recleaned, Reproven	(S88)
S75	Test Train, No. 10	Recleaned, Reproven	(S121)
S77	Test Train, No. 12	Recleaned, Reproven	(S106)
S90	Blank Train, No. 6	Recleaned, Reproven	(S105)
S95	Test Probe, No. 5G	Recleaned, Reproven	(S134)
S99	Florisil Trap, No. 23	Pentane Rinse, Not Reproven	
S101	Florisil Trap, No. 25	Recleaned, Reproven	(S127)
S102	Florisil Trap, No. 26	Recleaned, Reproven	(S128)
S118	Test Probe, No. 5A	Pentane Rinse, Not Reproven	(S159)
S121	Test Train, No. 10	Pentane Rinse, Not Reproven	(S157)
S122	Test Train, No. 15	Pentane Rinse, Not Reproven	(S158)
S130	Test Train, No. 18	Pentane Rinse, Not Reproven	(S176)
S139	Test Train, No. 20	Pentane Rinse, Not Reproven	
S141	Frits, No. 1, 2, 3	Pentane Rinse, Not Reproven	(S173)
S142	Frits, No. 4, 5	Pentane Rinse, Not Reproven	(S173)
S186	Test Train, No. 25	Pentane Rinse, Not Reproven	(S216)
S187	Test Train, No. 26	Pentane Rinse, Not Reproven	(S217)
S194	Test Train, No. 27	Pentane Rinse, Not Reproven	(S240)
S195	Test Train, No. 28	Pentane Rinse, Not Reproven	(S241)
S196	Blank Train, No. 13	Pentane Rinse, Not Reproven	
S235	Florisil Trap, No. 59	Pentane Rinse, Not Reproven	(S260)
S255	Blank Train, No. 16	Pentane Rinse, Not Reproven	

ORF

TABLE 4

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU BOILER TEST PARAMETERS

Test Number	Overfire Air	Nominal Steam Load kg/h
1	Low	31,780
4	High	18,160
5	High	31,780
6	Medium	31,780
7	High	31,780
8	Medium	31,780
9	Low	31,780
10	Low	18,160
11	Medium	31,780
12	Low	18,160
13	Low	31,780
14	Medium	31,780
15	High	18,160

TABLE 5

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
IDENTIFICATION OF DIOXIN TRAIN SAMPLING EQUIPMENT

Test Number	Sampling Probe		Sampling Train		Florisil Traps	
	Identification Number	Proving Analysis Number	Identification Number	Proving Analysis Number	Identification Numbers	Proving Analysis Numbers
1	5A	S31	1	S13	1, 2	S17, S18
2	5B	S32	2	S14	3, 4	S19, S20
3	5A	S88	5	S25	9,13	S40, S44
4	5H	S96	7	S27	15,14	S46, S45
5	5G	S95	9	S67	19,18	S79, S80
6	5A	S116	13	S97	24,22	S100, S83
7	5B	S114	12	S106	31,32	S131, S132
8	5E	S104	15	S122	30,29	S113, S112
9	5A	S146	16	S126	39,38	S163, S162
10	5D	S165	21	S151	33,34	S148, S149
11	5F	S199	18	S176	45,23	S190, S99
12	5A	S191	23	S167	53,55	S218, S220
13	5D	S198	25	S186	46,47	S202, S203
14	5A	S251	27	S194	50,51	S206, S207
15	5F	S226	29	S209	61,60	S237, S236

TABLE 6

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
IDENTIFICATION OF PCB TRAIN SAMPLING EQUIPMENT

Test Number	Sampling Probe		Sampling Train		Florisil Traps	
	Identification Number	Proving Analysis Number	Identification Number	Proving Analysis Number	Identification Numbers	Proving Analysis Numbers
1	5C	S33	3	S28	5, 6	S21, S22
2	5E	S35	4	S16	7, 8	S23, S24
3	5C	S87	6	S26	11,12	S42, S43
4	5D	S34	8	S65	17,16	S78, S47
5	5F	S94	11	S76	21,20	S82, S81
6	5C	S115	14	S98	25,26	S127,S128
7	5D	S119	10	S121	28,27	S111,S110
8	5H	S118	19	S117	36,37	S160,S161
9	5C	S145	17	S129	43,42	S177,S178
10	5F	S133	22	S152	35,44	S150,S189
11	5H	S183	20	S139	40,41	S171,S172
12	5C	S192	24	S175	56,54	S221,S219
13	5B	S164	26	S187	49,48	S205,S204
14	5C	S250	30	S210	52,58	S208,S234
15	5H	S227	28	S195	59,62	S235,S238

TABLE 7

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
IDENTIFICATION OF BLANK TRAIN SAMPLING EQUIPMENT

Test Number	Sampling Probe		Sampling Train		Florisil Traps	
	Identification Number	Proving Analysis Number	Identification Number	Proving Analysis Number	Identification Number	Proving Analysis Number
1	1	S36	1	S1	1	S5
2	-	-	-	-	-	-
3	-	-	-	-	-	-
4	4	S39	2	S2	2	S6
5	3	S38	3	S3	3	S7
6	2	S37	4	S4	4	S8
7	4	S120	5	S89	5	S49
8	5	S68	6	S105	6	S50
9	3	S135	8	S140	7	S51
10	2	S147	9	S143	8	S52
11	3	S166	7	S144	9	S53
12	4	S197	10	S153	10	S54
13	4	S225	11	S185	11	S55
14	4	S265	12	S188	12	S56
15	3	S252	13	S196	13	S57

TABLE 8

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
GAS VOLUME SAMPLED AND PARTICULATE MATERIAL COLLECTED - PCB TESTS

Test Number	Gas Volume Sampled* m^3	Particulate Material Collected		
		Main Filter mg	Probe Rinse** mg	Total mg
1	2.036	187.0	0.0	187.0
4	1.608	102.6	0.0	102.6
5	1.944	252.9	1058.9	1311.8
6	2.022	208.4	77.2	285.6
7	1.960	311.7	597.5	909.2
8	1.966	330.2	300.5	630.7
9	2.273	284.1	998.1	1282.2
10	2.109	153.0	173.2	326.2
11	2.083	236.7	373.0	609.7
12	1.969	77.5	15.0	92.5
13	2.244	368.1	587.4	955.5
14	1.296	161.7	43.1	204.8
15	1.747	88.5	47.9	136.4

* Dry Standard Conditions (1 Atmosphere, 25°C).

** In Test 1 and Test 4. the probe rinse was filtered through the main filter; in the remaining tests. the probe rinse was filtered through a separate filter.

TABLE 9

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
PARTICULATE CONCENTRATIONS AND EMISSION RATES*

Test Number	Average Sampling Train Oven Temperature		Particulate** Concentration		Particulate Emission Rate	
	Dioxin Train °C	PCB Train °C	Dioxin Train mg/m^3	PCB Train mg/m^3	Dioxin Train g/s	PCB Train g/s
1	121	118	101	92	1.59	1.51
4	118	117	27	64	0.38	0.89
5	121	117	51	675	0.81	10.94
6	123	120	271	141	4.70	2.39
7	118	117	371	464	5.78	7.91
8	121	118	400	321	6.95	5.53
9	118	120	159	564	3.04	11.05
10	122	121	62	155	1.06	2.77
11	119	118	116	293	1.94	5.03
12	119	119	61	47	1.02	0.79
13	119	113	85	426	1.50	7.93
14	121	118	163	158	2.83	2.76
15	121	118	61	78	0.91	1.17

* The particulate material recovery procedures were not the same for the dioxin and PCB trains. Therefore, the emission parameters for each test can be expected to differ.

** Dry, Reference (1 Atmosphere, 25°C).

TABLE 10

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
ISOKINETICITY - DIOXIN TESTS

Test Number	Number of Increments Sampled*	Average Percentage of Isokineticity	No. of Increments More Than 110% of Isokineticity	No. of Increments Less Than 90% of Isokineticity
1	96	101.99	7	2
4	96	98.09	2	9
5	96	103.21	7	2
6	96	99.44	5	10
7	96	95.88	2	11
8	96	92.39	0	9**
9	96	96.16	3	6
10	96	96.46	0	1
11	96	99.47	1	1
12	96	95.58	0	13
13	96	98.18	0	0
14	63	96.19	0	2***
15	96	95.13	0	2

* No. of Sampling Points X No. of Readings per Point.
** Filter Plugged Towards End of Third Traverse.
*** Only Two Stack Traverses Sampled.

TABLE 11

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU ISOKINETICITY - PCB TESTS

Test Number	Number of Increments Sampled*	Average Percentage of Isokineticity	No. of Increments More Than 110% of Isokineticity	No. of Increments Less Than 90% of Isokineticity
1	96	103.54	13	3
4	96	96.94	2	10
5	96	100.47	1	0
6	96	99.76	3	2
7	96	96.21	4	14
8	96	95.28	2	10**
9	96	96.92	0	4
10	96	98.64	2	5
11	96	101.20	3	1
12	96	97.88	1	4
13	96	100.65	0	2
14	60	99.09	0	2***
15	96	97.48	1	7

* No. of Sampling Points X No. of Readings per Point.
** Filter Plugged Towards End of Third Traverse.
*** Only Two Stack Traverses Sampled.

TABLE 12

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
STACK GAS PHYSICAL PARAMETERS - DIOXIN TESTS

Test Number	Absolute Static Pressure kPa	Molecular Weight, Dry Basis	Moisture Content % Vol.	Stack Gas Velocity m/s	Stack Gas Temperature °C	Stack Gas Flowrate	
						Actual m^3/s	Dry, Standard m^3/s*
1	101.17	30.40	12.5	8.856	286.10	33.7	15.7
4	100.51	30.36	11.1	7.285	241.48	27.7	14.2
5	101.22	29.80	17.6	9.610	290.50	36.6	15.9
6	102.38	30.20	15.7	10.556	316.19	40.2	17.3
7	102.58	30.04	13.3	8.884	295.07	33.8	15.6
8	99.53	30.12	13.8	10.515	308.38	40.0	17.4
9	102.85	28.97	14.5	11.399	314.45	43.4	19.1
10	102.78	29.68	11.3	9.029	268.80	34.3	17.0
11	102.78	29.68	14.2	9.657	296.46	36.7	16.7
12	102.41	29.48	12.0	8.903	263.42	33.9	16.7
13	101.70	29.67	15.6	10.859	316.89	41.3	17.7
14	101.50	29.73	16.4	10.705	311.23	40.7	17.4
15	101.77	29.55	11.9	7.769	250.25	29.5	14.9

* 1 Atmosphere, 25°C.

TABLE 13

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
STACK GAS PHYSICAL PARAMETERS - PCB TESTS

Test Number	Absolute Static Pressure kPa	Molecular Weight, Dry Basis	Moisture Content % Vol.	Stack Gas Velocity m/s	Stack Gas Temperature ^oC	Stack Gas Flowrate	
						Actual m^3/s	Dry, Standard m^3/s*
1	101.17	30.40	12.1	9.180	281.97	34.9	16.5
4	100.51	30.36	10.6	7.216	249.87	27.4	13.9
5	101.22	29.80	14.5	9.613	303.46	36.6	16.2
6	102.38	30.20	15.7	10.317	315.56	39.2	16.9
7	102.58	30.04	12.5	9.702	299.41	36.9	17.0
8	99.53	30.12	13.9	10.469	310.98	39.8	17.2
9	102.85	28.97	13.6	11.763	324.35	44.7	19.6
10	102.78	29.68	11.4	9.548	272.10	36.3	17.9
11	102.78	29.68	14.1	9.998	302.13	38.0	17.2
12	102.41	29.48	12.0	9.041	270.19	34.4	16.8
13	101.70	29.67	15.6	11.470	319.61	43.6	18.6
14	101.50	29.73	15.8	10.874	322.69	41.4	17.5
15	101.77	29.55	12.7	7.981	257.18	30.4	15.0

* 1 Atmosphere, 25^{o}C.

TABLE 14

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

DIOXIN SPIKE RECOVERIES FOR STACK GAS SAMPLES

Test Number	Dioxin Spike Recovery, %							
	Filter*		Impingers		Florisil No.1		Florisil No.2	
	Tetra	Octa	Tetra	Octa	Tetra	Octa	Tetra	Octa
1	35	19	72	72	45	24	52	21
4	53	50	74	59	80	11	86	37
5	110	94	31	16	25	35	34	14
6	17	27	76	25	50	39	45	71
7	57	52	110	83	52	40	33	68
8	95	36	63	150	55	43	108	120
9	41	37	96	85	44	8	25	7
10	48	27	30	16	74	12	15	130
11	27	11	112	43	44	20	20	4
12	60	25	55	48	85	24	111	42
13	41	30	27	26	58	81	58	24
14	63	70	124	12	53	44	140	49
15	59	28	49	20	69	25	129	79

* First 16 hr. soxhlet extraction only. Spike recoveries were insignificant during the second 16 hr. soxhlet extraction.

TABLE 15

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
QUANTITIES OF DIOXIN DETECTED IN TRAIN SAMPLES

Test Number	Dioxin Congener Collected, ng.					
	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Total
1	1100	1200	900	960	490	4650
4	580	830	1100	440	540	3490
5	1400	1600	1800	780	860	6440
6	4200	2900	1800	320	320	9540
7	870	1400	1900	740	330	5240
8	690	500	540	300	170	2200
9	1000	760	880	230	220	3090
10	970	960	930	390	290	3540
11	650	720	680	370	160	2580
12	1100	1200	1600	500	390	4790
13	730	650	640	160	180	2360
14	3600	2700	2000	680	490	9470
15	820	1300	1500	1200	1000	5820

TABLE 16

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
QUANTITIES OF FURAN DETECTED IN TRAIN SAMPLES

Test Number	Furan Congener Collected, ng.					
	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Total
1	6800	5700	2200	1700	320	16720
4	1700	1900	1200	90	90	4980
5	7900	7400	3400	1400	120	20220
6	10000	8100	2500	60	60	20720
7	4200	7100	3800	170	130	15400
8	3200	2300	1000	70	40	6610
9	5500	3400	1900	60	30	10890
10	3800	1700	1200	70	50	6820
11	4500	3300	1600	130	30	9560
12	3300	3300	2200	110	100	9010
13	4800	3700	1600	50	50	10200
14	4700	4100	1400	420	50	10670
15	2900	3300	2100	320	290	8910

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TABLE 17

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
DISTRIBUTION OF DIOXINS AND FURANS IN THE SAMPLING TRAINS

Test Number	Filter ng		Impinger Soln. ng		Florisil 1 ng		Florisil 2 ng		Total ng	
	Dioxin	Furan	Dioxin	Furan	Dioxin	Furan	Dioxin	Furan	Dioxin	Furan
1	2790	7860	1630	7690	210	1060	20	70	4650	16680
4	770	760	2320	3640	360	500	20	30	3470	4930
5	2250	5050	3880	13870	310	1200	20	90	6460	20210
6	8770	19060	720	1660	80	160	10	20	9580	20900
7	3670	8520	1400	6510	140	400	10	40	5220	15470
8	1030	2340	820	2910	330	1340	20	80	2200	6670
9	2880	9410	190	1210	40	270	0	0	3110	10890
10	730	910	2010	3820	410	730	400	1320	3550	6780
11	1800	6430	510	2510	170	180	90	440	2570	9560
12	560	590	3840	7430	430	950	30	60	4860	9030
13	1750	7000	440	2290	170	920	0	10	2360	10220
14	4290	5330	4970	5170	180	210	0	0	9440	10710
15	950	920	4670	7460	280	520	10	20	5910	8920

TABLE 18

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

QUANTITIES OF CHLOROBENZENES, PCB'S AND CHLOROPHENOLS DETECTED IN TRAIN SAMPLES

Test Number	Quantity Detected		
	Chlorobenzenes µg	PCB's ng	Chlorophenols µg
1	110	370	85
4	39	160	37
5	15	630	140
6	62	180	74
7	150	560	94
8	61	170	78
9	120	460	190
10	47	210	158
11	99	4300	67
12	68	1200	190
13	230	2100	230
14	55	450	6.2
15	46	1200	150

TABLE 19

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

DIOXIN SPIKE RECOVERIES FOR PROCESS SAMPLES

Test Number	Dioxin Spike Recovery, %					
	Refuse		Bottom Ash		Precipitator Ash	
	Tetra	Octa	Tetra	Octa	Tetra	Octa
1	4	11	45	43	190	130
4	10	11	330	26	170	390
5	29	34	39	76	150	1000
6	30	55	NA	NA	260	330
7	28	56	16	65	330	590
8	22	33	130	220	51	120
9	25	45	270	116	86	60
10	16	8	75	13	97	150
11	22	16	72	51	98	160
12	7	7	260	103	130	150
13	1	3	130	71	120	130
14	14	14	72	9	72	77
15	12	10	98	48	59	42

NA = Not Analysed.

TABLE 20

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
ANALYSIS OF PROCESS SAMPLES FOR CHLOROBENZENES, PCBs AND CHLOROPHENOLS

Test Number	Refuse			Bottom Ash			Precipitator Ash		
	Chloro-Benzenes ng	PCB's ng	Chloro-Phenols ng	Chloro-Benzenes ng	PCB's ng	Chloro-Phenols ng	Chloro-Benzenes ng	PCB's ng	Chloro-Phenols ng
1	330	900	12000	55	100	150	1000	200	ND
4	400	500	13000	ND	25	ND	220	170	12000
5	180	40000	6400	ND	15	150	120	140	1300
6	190	810	7600	ND	20	ND	120	20	750
7	2200	1500	15000	10	15	ND	130	45	1100
8	480	350	50	ND	10	50	220	110	800
9	500	320	8800	ND	ND	150	160	20	ND
10	210	350	11000	ND	ND	75	80	45	2600
11	460	1300	32000	ND	20	300	50	ND	850
12	480	610	18000	40	10	250	100	ND	1300
13	290	2500	37000	ND	15	500	56	50	1500
14	1200	860	100000	ND	ND	100	150	20	5000
15	1300	1900	78000	ND	20	200	310	85	1000

ND = None Detected.

TABLE 21

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
COMPARISON OF STACK GAS SAMPLE VOLUME MEASUREMENTS

Test Number	Stack Gas Sample Volume*, m^3	
	Dioxin Train	PCB Train
1	1.915	2.036
4	1.665	1.608
5	1.970	1.944
6	2.064	2.022
7	1.791	1.960
8	1.922	1.966
9	2.204	2.273
10	1.965	2.109
11	1.996	2.083
12	1.918	1.969
13	2.082	2.244
14	1.318	1.296
15	1.870	1.747

* Dry, Standard Conditions (1 Atmosphere, 25°C).

TABLE 22

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

TOTAL CONTAMINANT CONCENTRATIONS

Test Number	Contaminant Concentration*				
	Dioxins $\mu g/m^3$	Furans $\mu g/m^3$	Chlorobenzenes $\mu g/m^3$	PCB's ng/m^3	Chlorophenols $\mu g/m^3$
1	2.43	8.73	54.0	181.7	41.7
4	2.10	2.99	24.3	99.5	23.0
5	3.27	10.26	7.7	324.1	72.0
6	4.62	10.04	30.7	89.0	36.6
7	2.93	8.60	76.5	285.7	48.0
8	1.15	3.44	31.0	86.5	39.7
9	1.40	4.94	52.8	202.4	83.6
10	1.80	3.47	22.3	99.6	74.9
11	1.29	4.79	47.5	2064.3	32.2
12	2.50	4.70	34.5	609.4	96.5
13	1.13	4.90	102.5	935.8	102.5
14	7.19	8.10	42.4	347.2	4.8
15	3.11	4.77	26.3	686.9	85.9

* Dry standard conditions (1 Atmosphere, 25°C)

TABLE 23

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

STACK GAS DIOXIN CONGENER CONCENTRATIONS

Test Number	Congener Concentration, µg/m^{3}*				
	Tetra	Penta	Hexa	Hepta	Octa
1	0.57	0.63	0.47	0.50	0.26
4	0.35	0.50	0.66	0.26	0.32
5	0.71	0.81	0.91	0.40	0.44
6	2.04	1.41	0.87	0.16	0.16
7	0.49	0.78	1.06	0.41	0.18
8	0.36	0.26	0.28	0.16	0.09
9	0.45	0.35	0.40	0.10	0.10
10	0.49	0.49	0.47	0.20	0.15
11	0.33	0.36	0.34	0.19	0.08
12	0.57	0.63	0.83	0.26	0.20
13	0.35	0.31	0.31	0.08	0.09
14	2.73	2.05	1.52	0.52	0.37
15	0.44	0.70	0.80	0.64	0.54

* Dry, standard conditions (1 Atmosphere, 25°C).

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TABLE 24

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

STACK GAS FURAN CONGENER CONCENTRATIONS

Test Number	Congener Concentration, µg/m³*				
	Tetra	Penta	Hexa	Hepta	Octa
1	3.55	2.98	1.15	0.88	0.17
4	1.02	1.14	0.72	0.05	0.05
5	4.01	3.76	1.73	0.71	0.06
6	4.85	3.92	1.21	0.03	0.03
7	2.35	3.96	2.12	0.10	0.02
8	1.67	1.20	0.52	0.04	0.04
9	2.50	1.54	0.86	0.03	0.01
10	1.93	0.87	0.61	0.04	0.03
11	2.26	1.65	0.80	0.07	0.02
12	1.72	1.72	1.15	0.06	0.05
13	2.31	1.78	0.77	0.02	0.02
14	3.57	3.11	1.06	0.32	0.04
15	1.55	1.77	1.12	0.17	0.16

* Dry, standard conditions (1 atmosphere, 25°C)

TABLE 25

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

COMPARISON BETWEEN SAMPLE AND BLANK DIOXIN TRAIN RECOVERIES

Test Number	Sample Train Recovery		Blank Train Recovery		Relative Blank Recovery*	
	Dioxins ng	Furans ng	Dioxins ng	Furans ng	Dioxins %	Furans %
1	4650	16720	9	20	0.19	0.12
4	3490	4980	1	1	<0.01	<0.01
5	6440	20220	<1	<1	<0.01	<0.01
6	9540	20720	1	2	<0.01	0.01
7	5240	15400	<1	<1	<0.01	<0.01
8	2200	6610	37	160	1.68	2.42
9	3090	10890	7	20	0.23	0.18
10	3540	6820	<1	4	<0.01	0.06
11	2580	9560	<1	<1	<0.01	<0.01
12	4790	9010	3	14	0.06	0.16
13	2360	10200	1	8	<0.01	0.08
14	9470	10670	<1	4	<0.01	0.04
15	5820	8910	84	66	1.44	0.74

* Blank Recovery as a Percentage of Sample Recovery.

TABLE 26

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
COMPARISON OF STACK GAS FLOWRATE MEASUREMENTS

Test Number	Stack Gas Flowrate*, m^3/s	
	Dioxin Train	PCB Train
1	15.7	16.5
4	14.2	13.9
5	15.9	16.2
6	17.3	16.9
7	15.6	17.0
8	17.4	17.2
9	19.1	19.6
10	17.0	17.9
11	16.7	17.2
12	16.7	16.8
13	17.7	18.6
14	17.4	17.5
15	14.9	15.0

* Dry, Standard Conditions (1 Atmosphere, 25°C).

TABLE 27

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

TOTAL CONTAMINANT EMISSION RATES

Test Number	Contaminant Emission Rates				
	Dioxins µg/s	Furans µg/s	Chlorobenzenes µg/s	PCB's µg/s	Chlorophenols µg/s
1	38.15	137.06	891	3.00	689
4	29.82	42.46	337	1.38	320
5	51.99	163.13	125	5.25	1167
6	79.93	173.69	518	1.50	619
7	45.71	134.16	1301	4.86	815
8	20.01	60.03	534	1.49	683
9	26.74	94.35	1035	3.97	1638
10	30.60	58.99	399	1.78	1341
11	21.54	79.99	818	35.51	553
12	41.75	78.49	580	10.24	1621
13	20.00	86.73	1907	17.41	1907
14	125.11	140.94	743	6.08	84
15	46.34	71.07	395	10.30	1288

TABLE 28

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

STACK GAS DIOXIN CONGENER EMISSION RATES

Test Number	Congener Emission Rate, μg/s				
	Tetra	Penta	Hexa	Hepta	Octa
1	8.95	9.89	7.38	7.85	4.08
4	4.97	7.10	9.37	3.69	4.54
5	11.29	12.88	14.47	6.36	7.00
6	35.29	24.39	15.05	2.77	2.77
7	7.64	12.17	16.54	6.40	2.81
8	6.26	4.52	4.87	2.78	1.57
9	8.60	6.69	7.64	1.70	1.91
10	8.33	8.33	7.99	3.40	2.55
11	5.51	6.01	5.68	3.17	1.34
12	9.52	10.52	13.86	4.34	3.34
13	6.20	5.49	5.49	1.42	1.59
14	47.50	35.67	26.45	9.05	6.44
15	6.56	10.43	11.92	9.54	8.05

TABLE 29

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

STACK GAS FURAN CONGENER EMISSION RATES

Test Number	Congener Emission Rate, µg/s				
	Tetra	Penta	Hexa	Hepta	Octa
1	55.74	46.79	18.06	13.82	2.67
4	14.48	16.19	10.22	0.71	0.71
5	63.76	59.78	27.51	11.29	0.95
6	83.91	67.82	20.93	0.52	0.52
7	36.66	61.78	33.07	1.56	1.09
8	29.06	20.88	9.05	0.70	0.34
9	47.75	29.41	16.43	0.57	0.19
10	32.81	14.79	10.37	0.68	0.51
11	37.74	27.56	13.36	1.17	0.33
12	28.72	28.72	19.21	1.00	0.84
13	40.89	31.51	13.63	0.35	0.35
14	62.12	54.11	18.44	5.57	0.70
15	23.10	26.37	16.69	2.53	2.38

TABLE 30

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

REFUSE CONTAMINANT CONCENTRATIONS

Test Number	Contaminant Concentration				
	Dioxins ng/g	Furans ng/g	Chlorobenzenes ng/g	PCB's ng/g	Chlorophenols ng/g
1	8.8	25.0	6.6	18.0	240
4	10.3	ND	8.0	10.0	260
5	4.0	4.0	3.6	800.0	128
6	3.7	ND	3.8	16.2	152
7	13.4	ND	44.0	30.0	300
8	6.5	ND	9.6	7.0	1
9	11.7	ND	10.0	6.4	176
10	17.3	ND	4.2	7.0	220
11	15.8	ND	9.2	26.0	640
12	9.6	ND	9.6	12.2	360
13	97.0	0.3	5.8	50.0	740
14	29.6	0.4	24.0	17.2	2000
15	29.8	ND	26.0	38.0	1560

ND = None Detected

ORF

TABLE 31

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

BOTTOM ASH CONTAMINANT CONCENTRATIONS

Test Number	Contaminant Concentration				
	Dioxins ng/g	Furans ng/g	Chlorobenzenes ng/g	PCB's ng/g	Chlorophenols ng/g
1	0.6	1.1	1.1	2.0	3.0
4	ND	ND	ND	0.5	ND
5	ND	ND	ND	0.3	3.0
6	NA	NA	ND	0.4	ND
7	ND	1.3	0.2	0.3	ND
8	0.7	ND	ND	0.2	1.0
9	0.4	0.4	ND	ND	3.0
10	0.1	ND	ND	ND	1.5
11	0.1	ND	ND	0.4	6.0
12	0.5	ND	0.8	0.2	5.0
13	0.1	ND	ND	0.3	10.0
14	3.3	3.9	ND	ND	2.0
15	0.4	ND	ND	0.4	4.0

ND = None Dectected; NA = Not Analysed

TABLE 32

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

PRECIPITATOR ASH CONTAMINANT CONCENTRATIONS

Test Number	Contaminant Concentration				
	Dioxins ng/g	Furans ng/g	Chlorobenzenes ng/g	PCB's ng/g	Chlorophenols ng/g
1	32.5	89	20.0	4.0	ND
4	94.2	105	4.4	3.4	240
5	33.3	70	2.4	2.8	26
6	11.2	31	2.4	0.4	15
7	14.4	54	2.6	0.9	22
8	9.5	49	4.4	2.2	16
9	7.7	24	3.2	0.4	ND
10	17.3	29	1.6	0.9	52
11	9.6	36	1.0	ND	17
12	16.9	22	2.0	ND	26
13	10.8	33	1.1	1.0	30
14	35.3	41	3.0	0.4	100
15	6.2	23	6.2	1.7	20

ND = None Detected.

ORF

TABLE 33

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
REFUSE DIOXIN AND FURAN CONGENER CONCENTRATIONS

Test Number	Dioxin Concentrations, ng/g					Furan Concentrations, ng/g				
	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Tetra-	Penta-	Hexa-	Hepta-	Octa-
1	0.5	ND	ND	0.3	8.0	ND	ND	ND	ND	25.0
4	2.0	1.0	ND	0.3	7.0	ND	ND	ND	ND	ND
5	ND	ND	ND	2.0	2.0	3.0	1.0	ND	ND	ND
6	0.1	ND	ND	0.6	3.0	ND	ND	ND	ND	ND
7	ND	ND	1.1	1.3	11.0	ND	ND	ND	ND	ND
8	ND	ND	0.1	0.6	5.8	ND	ND	ND	ND	ND
9	ND	ND	0.7	1.0	10.0	ND	ND	ND	ND	ND
10	ND	ND	ND	1.3	16.0	ND	ND	ND	ND	ND
11	ND	ND	ND	1.8	14.0	ND	ND	ND	ND	ND
12	ND	ND	ND	1.7	7.9	ND	ND	ND	ND	ND
13	ND	ND	ND	20.0	77.0	ND	ND	ND	ND	0.3
14	ND	ND	1.1	3.5	25.0	ND	ND	ND	0.3	0.1
15	ND	ND	0.1	0.7	29.0	ND	ND	ND	ND	ND

ND = None Detected.

TABLE 34

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
BOTTOM ASH DIOXIN AND FURAN CONGENER CONCENTRATIONS

Test Number	Dioxin Concentrations, ng/g					Furan Concentrations, ng/g				
	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Tetra-	Penta-	Hexa-	Hepta-	Octa-
1	0.1	ND	0.2	0.1	0.2	0.1	0.5	0.5	ND	ND
4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6	-	-	-	-	-	-	-	-	-	-
7	ND	ND	ND	ND	ND	0.3	0.6	0.4	ND	ND
8	0.7	ND	ND	ND	ND	ND	ND	ND	ND	ND
9	ND	ND	0.1	0.1	0.2	ND	0.1	0.2	0.1	ND
10	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
11	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
12	0.2	ND	ND	ND	0.3	ND	ND	ND	ND	ND
13	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
14	0.4	0.9	1.2	0.5	0.3	0.8	1.5	1.1	0.5	ND
15	0.1	ND	ND	0.1	0.2	ND	ND	ND	ND	ND

ND = None Detected.

TABLE 35

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
PRECIPITATOR ASH DIOXIN AND FURAN CONGENER CONCENTRATIONS

Test Number	Dioxin Concentrations, ng/g					Furan Concentrations, ng/g				
	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Tetra-	Penta-	Hexa-	Hepta-	Octa-
1	7.9	9.0	8.5	4.7	2.4	36.0	30.0	15.0	7.4	0.3
4	12.0	25.0	42.0	9.2	6.0	19.0	40.0	35.0	9.2	2.1
5	2.6	6.1	21.0	1.7	1.9	8.7	19.0	40.0	2.1	0.1
6	2.9	3.1	3.2	1.1	0.9	12.0	13.0	4.6	1.2	ND
7	2.6	4.5	4.2	1.3	1.8	10.0	19.0	22.0	2.3	0.6
8	2.7	3.7	2.7	0.2	0.2	14.0	22.0	12.0	0.8	ND
9	1.6	2.8	2.4	0.7	0.2	9.1	8.3	5.6	0.8	ND
10	2.3	5.2	6.7	2.0	1.1	5.1	11.0	10.0	2.3	0.1
11	1.8	3.4	3.6	0.6	0.2	9.4	15.0	10.0	1.3	ND
12	2.5	5.2	6.4	1.8	1.0	4.5	8.5	7.2	1.6	0.1
13	2.3	3.8	3.3	1.0	0.4	9.3	13.0	8.5	1.8	ND
14	4.6	9.7	13.0	4.9	3.1	8.1	15.0	12.0	5.3	0.2
15	1.7	2.0	1.5	0.5	0.5	8.8	9.5	3.9	0.9	ND

ND = None Detected.

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TABLE 36

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

STATISTICAL TEST FOR DIFFERENCES IN VOLUME SAMPLED AND FLOWRATES

Test Number	Volume Sampled, m^3			Flowrate, m^3/s		
	Dioxin Train (a)	PCB Train (b)	Difference (a-b)	Dioxin Train (a)	PCB Train (b)	Difference (a-b)
1	1.915	2.036	-0.121	15.7	16.5	-0.8
4	1.665	1.608	+0.057	14.2	13.9	+0.3
5	1.970	1.944	+0.026	15.9	16.2	-0.3
6	2.064	2.022	+0.042	17.3	16.9	+0.4
7	1.791	1.960	-0.169	15.6	17.0	-1.4
8	1.922	1.966	-0.044	17.4	17.2	+0.2
9	2.204	2.273	-0.069	19.1	19.6	-0.5
10	1.965	2.109	-0.144	17.0	17.9	-0.9
11	1.996	2.083	-0.087	16.7	17.2	-0.5
12	1.918	1.969	-0.051	16.7	16.8	-0.1
13	2.082	2.244	-0.162	17.7	18.6	-0.9
14	1.318	1.296	+0.022	17.4	17.5	-0.1
15	1.870	1.747	+0.123	14.9	15.0	-0.1
	Sum = -0.577 Average = -0.044 σ Overall = 0.113 σ Average = 0.031 t (calculated) = $\frac{0.044-0}{0.031}$ = 1.42 t(0.05,12) = 2.18 t(0.02,12) = 2.68			Sum = -4.7 Average = -0.36 σ Overall = 0.515 σ Average = 0.143 t (calculated) = $\frac{0.36-0}{0.143}$ = 2.52 t(0.05,12) = 2.18 t(0.02,12) = 2.68		

TABLE 37

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
CONFIDENCE RANGE FOR VOLUME OF STACK GAS SAMPLED DATA

Test Number	Volume Sampled, m^3		Difference, m^3
	Dioxin Train (a)	PCB Train (b)	(a-b)
1	1.915	2.036	0.121
4	1.665	1.608	0.057
5	1.970	1.944	0.026
6	2.064	2.022	0.042
7	1.791	1.960	0.169
8	1.922	1.966	0.044
9	2.204	2.273	0.069
10	1.965	2.109	0.144
11	1.966	2.083	0.087
12	1.918	1.969	0.051
13	2.082	2.244	0.162
14	1.318	1.296	0.022
15	1.870	1.747	0.123
			Mean 0.086
Confidence Range = 1.737 (a-b) = 0.149m^3.			

TABLE 38

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
CONFIDENCE RANGE FOR STACK GAS FLOWRATE DATA

Test Number	Flowrate, m^3/s		Difference, m^3/s
	Dioxin Train (a)	PCB Train (b)	(a-b)
1	15.7	16.5	0.8
4	14.2	13.9	0.3
5	15.9	16.2	0.3
6	17.3	16.9	0.4
7	15.6	17.0	1.4
8	17.4	17.2	0.2
9	19.1	19.6	0.5
10	17.0	17.9	0.9
11	16.7	17.2	0.5
12	16.7	16.8	0.1
13	17.7	18.6	0.9
14	17.4	17.5	0.1
15	14.9	15.0	0.1
			Mean 0.5
Confidence Range = 1.737 (a-b) = $0.87 m^3/s$.			

TABLE 39

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
CONFIDENCE RANGES FOR DIOXIN AND FURAN ANALYSES

(a) DIOXIN ANALYSES

Test Number	Impinger Analysis, ng		Difference, ng
	Analysis 1 (a)	Analysis 2 (b)	(a-b)
8	824	625	199
11	511	476	35
13	441	416	25
Mean	592	506	86

Confidence Range = 1.737 (a-b) = 149 ng.

(b) FURAN ANALYSES

Test Number	Impinger Analysis, ng		Difference, ng
	Analysis 1 (a)	Analysis 2 (b)	(a-b)
8	2912	2617	295
11	2505	3065	560
13	2293	2316	23
Mean	2570	2666	293

Confidence Range = 1.737 (a-b) = 509 ng.

ORF

TABLE 40

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

CONFIDENCE RANGES FOR CHLOROBENZENE, PCB AND CHLOROPHENOL ANALYSES

(a) Chlorobenzene Analysis

Average Analytical Result = 100 ng
Average Standard Deviation, σ = 4.33 ng

Confidence Range = 1.960σ = 8.49 ng

(b) PCB Analysis

Average Analytical Result = 3000 ng
Average Standard Deviation, σ = 3.8 ng

Confidence Range = 1.960σ = 7.45 ng

(c) Chlorophenol Analysis

Average Analytical Result = 833 ng
Average Standard Deviation, σ = 8.65 ng

Confidence Range = 1.960σ = 16.95 ng

ORF

TABLE 41

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
CONFIDENCE RANGES FOR CONTAMINANT CONCENTRATIONS AND EMISSION RATES

Contaminant	Concentration	Emission Rate
Dioxin	$CR^2 = (7.76)^2 + (27.14)^2$, $CR = 28.22\%$	$CR^2 = (5.19)^2 + (28.22)^2$, $CR = 28.69\%$
Furan	$CR^2 = (7.76)^2 + (19.44)^2$, $CR = 20.93\%$	$CR^2 = (5.19)^2 + (20.93)^2$, $CR = 21.56\%$
Chlorobenzene	$CR^2 = (7.76)^2 + (8.49)^2$, $CR = 11.50\%$	$CR^2 = (5.19)^2 + (11.50)^2$, $CR = 12.62\%$
PCB	$CR^2 = (7.76)^2 + (0.25)^2$, $CR = 7.76\%$	$CR^2 = (5.19)^2 + (7.76)^2$, $CR = 9.34\%$
Chlorophenol	$CR^2 = (7.76)^2 + (2.03)^2$, $CR = 8.02\%$	$CR^2 = (5.19)^2 + (8.02)^2$, $CR = 9.55\%$

CR = Confidence Range

TABLE 42

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU
CONFIDENCE RANGES FOR INDIVIDUAL CONTAMINANT CONCENTRATIONS

Test Number	Contaminant Concentration*				
	Dioxins µg/m³	Furans µg/m³	Chlorobenzenes µg/m³	PCB's ng/m³	Chlorophenols µg/m³
1	2.43 ± 0.69	8.73 ± 1.83	54.0 ± 6.2	181.7 ± 14.1	41.7 ± 3.3
4	2.10 ± 0.59	2.99 ± 0.63	24.3 ± 2.8	99.5 ± 7.7	23.0 ± 1.8
5	3.27 ± 0.92	10.26 ± 2.15	7.7 ± 0.9	324.1 ± 25.2	72.0 ± 5.8
6	4.62 ± 1.30	10.04 ± 2.10	30.7 ± 3.5	89.0 ± 6.9	36.6 ± 2.9
7	2.93 ± 0.83	8.60 ± 1.80	76.5 ± 8.8	285.7 ± 22.2	48.0 ± 3.8
8	1.15 ± 0.32	3.44 ± 0.72	31.0 ± 3.6	86.5 ± 6.7	39.7 ± 3.2
9	1.40 ± 0.40	4.94 ± 1.03	52.8 ± 6.1	202.4 ± 15.7	83.6 ± 6.7
10	1.80 ± 0.51	3.47 ± 0.73	22.3 ± 2.6	99.6 ± 7.7	74.9 ± 6.0
11	1.29 ± 0.36	4.79 ± 1.00	47.5 ± 5.5	2064.3 ± 160.2	32.2 ± 2.6
12	2.50 ± 0.71	4.70 ± 0.98	34.5 ± 4.0	609.4 ± 47.3	96.5 ± 7.7
13	1.13 ± 0.32	4.90 ± 1.03	102.5 ± 11.8	935.8 ± 72.6	102.5 ± 8.2
14	7.19 ± 2.03	8.10 ± 1.70	42.4 ± 4.9	347.2 ± 26.9	4.8 ± 0.4
15	3.11 ± 0.88	4.77 ± 1.00	26.3 ± 3.0	686.9 ± 53.3	85.9 ± 6.9

*Dry Standard Conditions (1 Atmosphere, 25°C)

TABLE 43

TRACE ORGANIC CONTAMINANT SAMPLING AT SWARU

CONFIDENCE RANGES FOR INDIVIDUAL CONTAMINANT EMISSION RATES

Test Number	Contaminant Emission Rate				
	Dioxins µg/s	Furans µg/s	Chlorobenzenes µg/s	PCB's µg/s	Chlorophenols µg/s
1	38.2 ± 11.0	137.1 ± 29.6	891 ± 112	3.00 ± 0.28	689 ± 66
4	29.8 ± 8.5	42.5 ± 9.2	337 ± 43	1.38 ± 0.13	320 ± 31
5	52.0 ± 14.9	163.1 ± 35.2	125 ± 16	5.25 ± 0.49	1167 ± 111
6	79.9 ± 22.9	173.7 ± 37.4	518 ± 65	1.50 ± 0.14	619 ± 59
7	45.7 ± 13.1	134.2 ± 28.9	1301 ± 164	4.86 ± 0.45	815 ± 78
8	20.0 ± 5.7	60.0 ± 12.9	534 ± 67	1.49 ± 0.14	683 ± 65
9	26.7 ± 7.7	94.4 ± 20.4	1035 ± 131	3.97 ± 0.37	1638 ± 156
10	30.6 ± 8.8	59.0 ± 12.7	399 ± 50	1.78 ± 0.17	1341 ± 128
11	21.5 ± 6.2	80.0 ± 17.2	818 ± 103	35.51 ± 3.32	553 ± 53
12	41.8 ± 12.0	78.5 ± 16.9	580 ± 73	10.24 ± 0.96	1621 ± 155
13	20.0 ± 5.7	86.7 ± 18.7	1907 ± 241	17.41 ± 1.63	1907 ± 182
14	125.1 ± 35.9	140.9 ± 30.4	743 ± 94	6.08 ± 0.57	84 ± 8
15	46.3 ± 13.3	71.1 ± 15.3	395 ± 50	10.30 ± 0.96	1288 ± 123

ORF

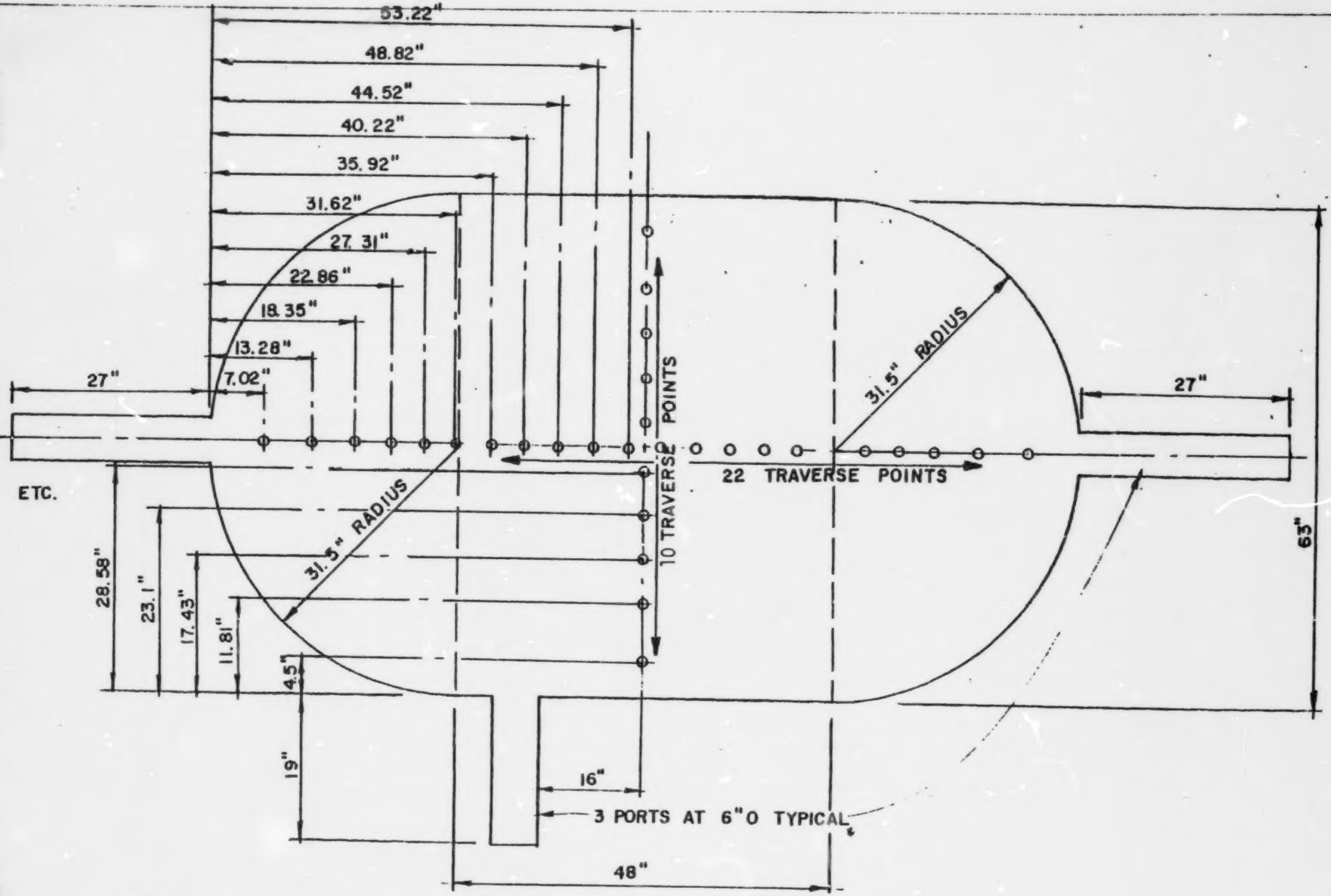
53.22"
48.82"
44.52"
40.22"
35.92"
31.62"
27.31"
22.86"
18.35"
13.28"
7.02"
27"
27"
31.5" RADIUS
31.5" RADIUS
10 TRAVERSE POINTS
22 TRAVERSE POINTS
ETC.
28.58"
23.1"
17.43"
11.81"
4.5"
19"
16"
3 PORTS AT 6" O TYPICAL
48"
63"

FIGURE 1: CROSS SECTION OF EXHAUST STACK AT THREE SAMPLING PORTS WITH EQUAL ELEMENTAL AREA TRAVERSE POINT LOCATIONS.

ORF

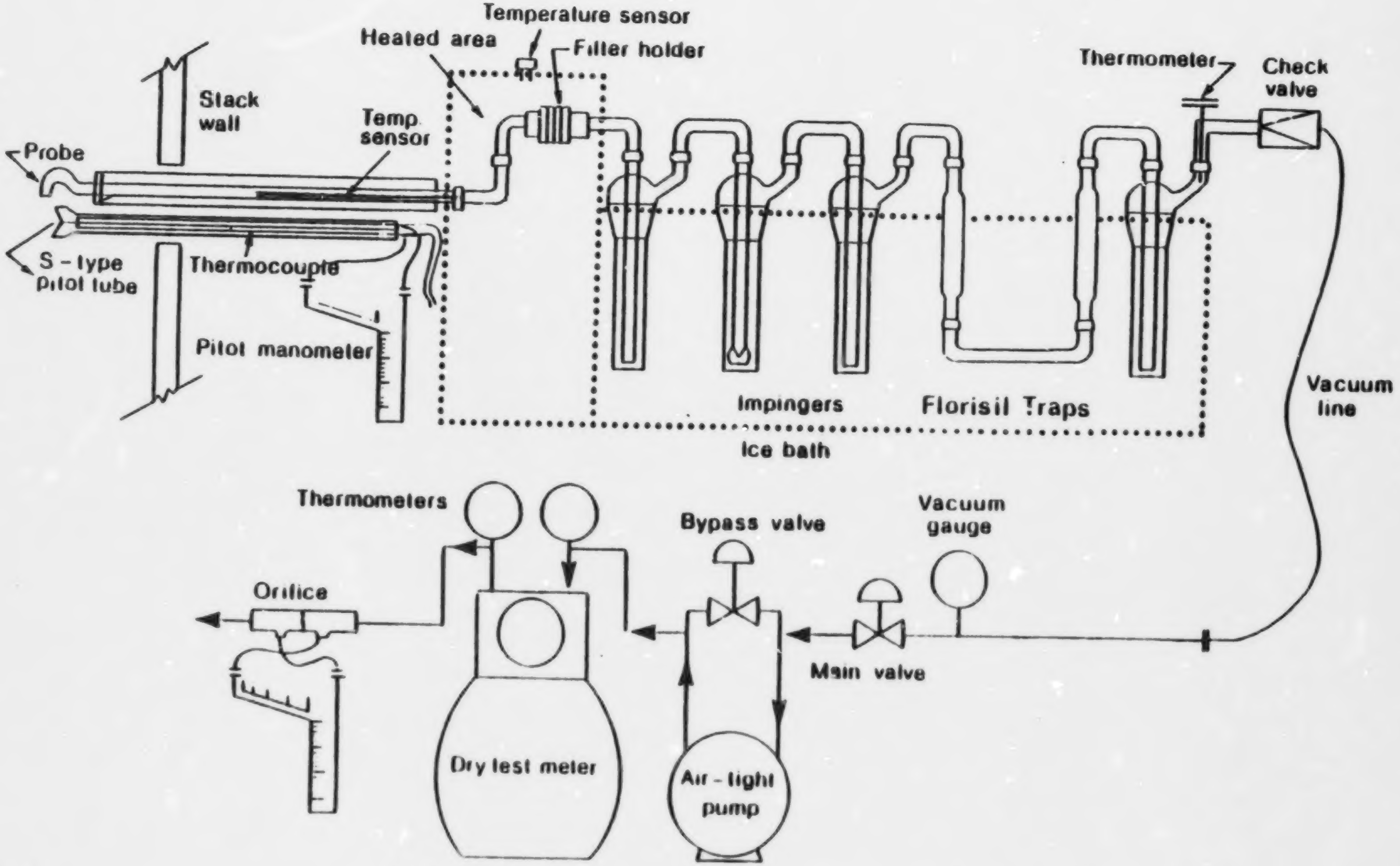
Temperature sensor
Heated area
Filter holder
Thermometer
Check valve
Stack wall
Temp. sensor
Probe
S - type pitot tube
Thermocouple
Pitot manometer
Impingers
Florisil Traps
Ice bath
Vacuum line
Thermometers
Vacuum gauge
Bypass valve
Orifice
Main valve
Dry test meter
Air - tight pump

FIGURE 2

TRACE ORGANIC SAMPLING TRAIN

APPENDIX(July 12,1984)

Standard Deviations Associated with Selected Results

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Train Component	Average Spike Recovery, % Tetra-Dioxin	Octa-Dioxin
Filter	54 (26)	39 (23)
Impingers	71 (33)	50 (40)
Florisil 1	56 (17)	31 (19)
Florisil 2	66 (44)	51 (41)
Average	62 (31)	43 (32)

( ) = Standard Deviation

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Train Component	Contaminant Distribution, % Dioxins	Furans
Filter	50.9 (28.2)	49.1 (29.0)
Impingers	43.2 (25.5)	43.8 (25.4)
Florisil 1	4.9 (4.3)	5.6 (5.4)
Florisil 2	1.0 (3.1)	1.5 (5.3)
Total	100.0	100.0

( ) = Standard Deviation

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	Contaminant % (Table 15, Table 16) Dioxins	Furans
Average	30 (9)	70 (9)

( ) = Standard Deviation

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Process Sample	Average Spike Recovery, %	
	Tetra-Dioxin	Octa-Dioxin
Refuse	17 (10)	23 (19)
Bottom Ash	128 (103)	70 (57)
Precipitator Ash	139 (82)	256 (272)
Average	95 (92)	116 (189)

( ) = Standard Deviation

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Contaminant Class	Average Concentration µg/m³	Concentration Range µg/m³	Concentration Relative to Dioxin
Dioxins	2.69 (1.69)	1.13 - 7.19	1.0
Furans	6.15 (2.61)	2.99 - 10.26	2.3
Chlorobenzenes	42.5 (25.1)	7.7 -102.5	15.8
PCB's	0.463 (0.549)	0.087 - 2.064	0.2
Chlorophenols	57.0 (30.6)	4.8 -102.5	21.2

( ) = Standard Deviation

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Congener	Congener Concentration		Relative Concentration	
	Dioxin µg/m³	Furan µg/m³	Dioxin %	Furan %
Tetra-	0.76 (0.74)	2.56 (1.11)	28.3	41.6
Penta-	0.71 (0.50)	2.26 (1.12)	26.4	36.8
Hexa-	0.69 (0.36)	1.06 (0.45)	25.7	17.2
Hepta-	0.30 (0.18)	0.21 (0.28)	11.1	3.4
Octa-	0.23 (0.15)	0.06 (0.05)	8.5	1.0
Total	2.69 (1.69)	6.15 (2.61)	100.0	100.0

( ) = Standard Deviation

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Contaminant Class	Average Emission Rate µg/s	Emission Rate Range µg/s	Emission Rate Relative to Dioxin
Dioxin	44.44 (29.32)	20.01 - 125.11	1.0
Furan	101.92 (42.91)	42.46 - 173.69	2.3
Chlorobenzene	737 (473)	125 - 1907	16.6
PCB's	7.91 (9.51)	1.38 - 35.51	0.2
Chlorophenol	979 (556)	84 - 1907	22.0

( ) = Standard Deviation

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Congener	Emission Rates			
	Dioxin µg/s	%	Furan µg/s	%
Tetra-	12.82 (13.04)	28.8	42.83 (19.23)	42.1
Penta-	11.85 (8.77)	26.7	37.36 (18.29)	36.7
Hexa-	11.29 (6.04)	25.4	17.46 (6.88)	17.2
Hepta-	4.81 (2.74)	10.8	3.11 (4.44)	3.1
Octa-	3.69 (2.22)	8.3	0.89 (0.77)	0.9
Total	44.46 (29.32)	100.0	101.65 (42.91)	100.0

( ) = Standard Deviation

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Contaminant Class	Average Concentration ng/g	Concentration Range ng/g
Dioxins	19.8 (24.6)	3.7 - 97.0
Furans	2.3 (6.9)	0.1 - 25.0
Chlorobenzenes	12.6 (11.8)	3.6 - 44.0
PCB's	79.8 (216.8)	6.4 - 800.0
Chlorophenols	521.3 (600.1)	1.0 - 2000.0

( ) = Standard Deviation

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Contaminant Class	Average Concentration ng/g	Concentration Range ng/g
Dioxins	0.5 (0.9)	0.1 - 3.3
Furans	0.6 (1.1)	0.1 - 3.9
Chlorobenzenes	0.2 (0.3)	0.1 - 1.1
PCB's	0.4 (0.5)	0.1 - 2.0
Chlorophenols	3.0 (2.8)	0.1 - 10.0

( ) = Standard Deviation

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Contaminant Class	Average Concentration ng/g	Concentration Range ng/g
Dioxins	23.0 (23.7)	6.2 - 94.2
Furans	47.0 (26.4)	22.0 - 105.0
Chlorobenzenes	4.2 (5.0)	1.0 - 20.0
PCB's	1.4 (1.3)	0.1 - 4.0
Chlorophenols	43.0 (64.4)	0.1 - 240.0

( ) = Standard Deviation

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Congener	Precipitator Ash Concentration			
	Dioxins ng/g	%	Furans ng/g	%
Tetra-	3.7 (3.0)	16	11.8 (8.1)	25
Penta-	6.4 (6.0)	28	17.2 (9.2)	37
Hexa-	9.1 (11.3)	40	14.3 (11.4)	31
Hepta-	2.3 (2.6)	10	2.8 (2.7)	6
Octa-	1.5 (1.6)	6	0.3 (0.6)	1
Total	23.0 (23.7)	100	46.4 (26.4)	100

( ) = Standard Deviation

ANALYSIS OF SWARU INCINERATOR COMBUSTION PRODUCTS FOR CHLORINATED ORGANIC COMPOUNDS

by

R. E. Clement
H. M. Tosine
J. Osborne

November, 1983

Ontario Ministry of the Environment
Laboratory Services and Applied Research Branch

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1. INTRODUCTION

From a 1982 study of the emissions of chlorinated organic compounds from Ontario municipal waste incinerators, it was found that the levels of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) from the stack exceeded the Ontario Provisional Guideline for PCDD/PCDF. To protect the health of the residents in the vicinity of the Swaru plant an immediate 20 percent cutback in the burning of waste was effected. Since this action, modifications to the plant's electrostatic precipitator system were made. To test the effectiveness of these modifications, and to determine the effect of incinerator operating conditions on emission levels, an expanded testing program was initiated. This testing program was designed to be a series of 16 stack and process sample tests performed in conjunction with combustion experiments. The diagnostic nature of this program may produce data which will indicate operating conditions that will minimize PCDD/PCDF emissions.

This report describes the analysis methods used to determine PCDD/PCDF concentrations in the various samples collected, and presents the analytical data obtained. Sampling of feedstock, stack vapour and particulates, precipitator fly-ash, and bottom ash was performed for each combustion test.

Modifications concerning the number of solvents used for extraction were made for these samples, since the most efficient extracting solvents were determined from the previous study and from the reported work of others. To obtain maximum efficiency for the extraction of PCDD/PCDF and for chlorophenols (CP), chlorobenzenes (CB) and polychlorinated biphenyls (PCB), two sampling trains were used for each stack test; one train was used to determine PCDD/PCDF compounds, the other was for the determination of other chlorinated species. Methods and results reported here are for work performed at the Laboratory Services and Applied Research Branch, Ministry of the Environment. Also, differences in the procedures used from those described in the Work Statement are described in this report. Methods used by Ontario Research Foundation personnel are only referenced or briefly described.

2. ANALYTICAL PROCEDURES

The sampling and analysis methods are described in detail in the Work Statement titled, "Stack Sampling for Trace Organic Contaminants (Version #5 - Swaru)". Procedures detailed in this report are for the analytical work performed at the Ministry of the Environment laboratories. Work performed by the Ontario Research Foundation and described in detail in the Work Statement is only briefly described here.

2.1 Sample Collection

Originally, 16 Tests were to be performed. However, two of the Tests were aborted due to operating problems at the incinerator and the last experiment was not conducted. Chronological numbering of the Tests is used in this report, from Test 1 to Test 15, with Tests 2 and 3 missing.

Stack samples were obtained using a modified U.S. Environmental Protection Agency (EPA) Method 5 sampling train. The principal modification by M.O.E. to the EPA design is the addition of two florisil cartridges after the third impinger. These cartrideges are in series and held in a vertical position.

Approximate sampling periods were four hours. Each hour during the stack sampling period, the feedstock, precipitator fly-ash, and bottom ash samples were collected. These 1-hour samples were individually composited to give four-hour samples corresponding to the four-hour stack sampling period. Two sampling trains were simultaneously operated for each Test; one was used for extraction and analysis of PCDD/PCDF compounds, the second was for the determination of PCB, CP and CB compounds. A blank train was operated on the stack sampling platform during leak-testing of the two sample trains. All stack sampling was performed by Ontario Research Foundation (ORF) personnel as described in the Work Statement. For each Test, the following samples were obtained:

A. Stack Samples:

1. filter and particulate catch-16 hour extraction
2. filter and particulate catch - 2nd 16 hour extraction
3. filter blank
4. impingers and contents
5. impinger blank
6. florisil cartridge #1
7. florisil cartridge #2
8. florisil blank

B. Process Samples:

9. precipitator fly-ash
10. bottom ash
11. feedstock

Support data such as initial filter weight, initial impinger volume and stack gas volume sampled were recorded by ORF personnel.

2.2 Sample Extraction

2.2.1 Glassware preparation. Each piece of glassware used was scrubbed with an aqueous detergent solution, rinsed once with deionized water, once with acetone, and stored until needed. Just prior to its use, the glassware was rinsed twice with methanol and fifteen times with methylene chloride. The last rinse of methylene chloride was collected for analysis by GC-Electron Capture Detection (ECD) to check for contamination. Further methylene chloride rinses were performed, if necessary, until no contamination was detected by GC-ECD.

The fritted glass fibre filter support discs used in the stack sampling train required more extensive cleaning procedures. They were consecutively extracted six times by ultrasonic agitation using 2 x methanol, 2 x acetone and 2 x methylene chloride solvents. Five minute extraction periods were employed.

2.2.2 Recovery from PCDD/PCDF sample train. Each stack sampling train was divided into four samples: the filter with trapped particulates, impingers and contents, and two florisil cartridges. Added to the filter was material recovered from the sampling probe by 3 pentane washes and particulates physically removed from the probe by brushing the interior in the presence of a pentane rinse. Connecting glassware from the probe and including the front half of the filter holder was also rinsed with pentane, and these rinsings included with the filter extract. After pentane rinsing of the probe and glassware, the procedure was repeated using methylene chloride solvent. Solvent rinsings were filtered through a fresh glass fibre filter to collect particulates to be extracted with those already collected by the train filter. Solvents were concentrated by rotary evaporation and added later to the toluene Soxhlet extract of the particulates.

Impingers and connecting glassware were rinsed several times using toluene. The fritted filter holder was extracted with 2 x 100 ml methylene chloride and 2 x 100 ml toluene in an ultrasonic bath, and these solvents added to the impinger glassware rinsings. After reducing the solvent volume by rotary evaporation, the rinsings were added to the solvent extract of the impinger contents. Procedures used by ORF personnel for recovery of sample from the CP, CB and PCB train were not identical to those described above, although very similar. Differences are described in the Work Statement.

2.2.3 Extraction of filter and trapped particulates for PCDD/PCDF. The filter and trapped particulates were weighed before extraction, although they were not pre-desiccated. After weighing, the filter was placed on top of a beaker having smaller diameter than the filter. Solutions of ^{13}C-2,3,7,8-TCDD and ^{13}C-OCDD were spiked on top of the filtered particulates so that the wetted portion did not contact the glass surface of the beaker. The beaker and filter were allowed to sit in a fume hood for 30 minutes before further treatment. Extraction of the filter and collected particulates was performed as follows:

1. The filter was placed in the bottom of a beaker, particulate side facing up, and enough 6 molar HCl was added to completely immerse the particulates (ca:100 ml). Particulates collected

from the probe and filtered from the probe rinses were added to the beaker.

2. This beaker was agitated in an ultrasonic bath for 30 minutes.

3. The aqueous solution was filtered through a clean glass fibre filter; the sample filter was transferred to this clean filter and rinsed with 100 to 200 ml distilled water.

4. Filtered particulates were air-dried overnight in a Petri dish, then extracted by Soxhlet for 16 hours with 200 ml toluene and a cycle time of 6 to 10 minutes.

5. Toluene extracts were concentrated to 5 to 10 ml by rotary evaporation and PCDD/PCDF compounds recovered by the clean-up procedure described in Appendix I. The final sample volume was 10 ul in isooctane solvent. Before clean-up, solvents from the probe and connecting glassware rinsing were added to the toluene extract.

6. The filter and particulates were extracted for a second 16 hours with a fresh 200 ml toluene as described above. This extract was treated and saved as a separate sample.

2.2.4 Fritted glass filter support and rear half of filter holder. The frit was extracted with 2 x 200 ml toluene and 2 x 200 ml methylene chloride by ultrasonic agitation. Extraction times were 20 minutes. Interior surfaces of the rear half of the filter holder were rinsed four times with pentane and these rinsings added to the frit extracts. These solvents were concentrated by rotary evaporation to about 10 ml and added to the solvent extracts of the impinger contents.

2.2.5 Extraction of impinger contents. The volume of impinger contents was recorded. Extraction was peformed using 800 ml aliquots of the impinger liquid as follows:

1. Four hundred ml of impinger solution were added to a volumetric flask with magnetic stirring bar. This solution was spiked with ^{13}C-2,3,7,8-TCDD and ^{13}C-OCDD. After adding an additional 400 ml of impinger liquid, 100 ml of toluene were added.

2. Extraction was performed by vigorous stirring for 30 minutes. After removing the toluene solvent, this procedure was repeated two additional times with fresh 100 ml portions of toluene.

3. Sample extracts were reduced to 5 to 10 ml by rotary evaporation and treated to recover PCDD/PCDF compounds as described in Appendix I. Final sample volume for GC/MS analysis was 50 ul in isooctane solvent.

2.2.6 Extraction of florisil cartridges. PCDD/PCDF compounds were recovered from florisil cartridges by direct solvent elution. Before addition of solvent, cartridges were vertically clamped and the glass wool packing removed from the top of the cartridge. ^{13}C-2,3,7,8-TCDD and ^{13}C-OCDD were added by microlitre syringe to the top of each cartridge to be extracted. Care was taken to spike the surface of the florisil adsorbent and avoid the glass walls of the cartridge. After letting stand for 30 minutes, the original glass wool plug was replaced and the cartridge eluted using 100 ml toluene by gravity flow. After reducing the eluant volume to about 5 ml by rotary evaporation, the sample was treated according to the procedure described in Appendix I. Final sample volumes for florisil extracts were 10 ul.

2.2.7 Sample recovery from PCB, CP and CB sampling train. Work for the recovery and extraction of PCB, CP and CB compounds from their sampling train was performed by ORF personnel. The methods used were generally similar to those described above for PCDD/PCDF compounds, but modifications were necessary to the procedures already described due to the appreciable volatility of many lower chlorinated PCB, CP and CB compounds. Toluene solvent was not used, only solvents which can be distilled at lower temperatures were employed. These solvents included pentane, acetone and methylene chloride. All sample concentrations were performed using Kuderna-Danish and Snyder apparatus. Before every solvent condensation, a keeper of about 1.0 ml isooctane was added. Particulate samples were treated with 6 molar HCl before extraction as previously described, and all concentrated extracts were treated to remove interferences as described in Appendix I. Detailed sample recovery and extraction procedures for the PCB, CP and CB train by ORF personnel are documented in the Work Statement. All sample clean-up was performed by Ministry of the Environment personnel. No spiking procedures were used for PCB, CP and CB extractions.

2.2.8 Extraction of process samples: Feedstock, Bottom Ash, Precipitator Fly-ash for PCDD/PCDF. The procedure for extraction of process samples for PCDD/PCDF compounds was the same as described for extraction of the filter and particulates in section 2.2.3. Ten gram aliquots of the composite samples supplied by ORF personnel were extracted.

Spiking was performed by spreading the sample over the bottom of a 250 ml beaker, and adding the spiking solutions to the surface of the particulate material. Direct contact of the spiking solution and glass wall of the beaker was avoided. Acid treatment with 6M HCl, filtering, air-drying and Soxhlet extraction of process samples using toluene were as described in section 2.2.3. Feedstock, bottom ash and fly-ash samples were spiked with ^{13}C-2,3,7,8-TCDD and ^{13}C-OCDD before extracting. After extraction, samples were concentrated by rotary evaporation and prepared for GC/MS analysis as described in Appendix I. Final sample volumes were 10 ul for feedstock and bottom ash extracts, and 100 ul for precipitator fly-ash extracts. Because of the very high levels of total organic material in feedstock samples, their extracts exceeded the capacity of the cleanup columns used and were put through a second set of columns.

2.3 Instrumental Analysis and Quantification Procedures

2.3.1 GC/MS analysis for PCDD/PCDF. All PCDD/PCDF quantifications were performed using data from high resolution gas chromatography - low resolution mass spectrometry (GC/MS) analyses. A Finnigan 4500 GC/MS with Incos data system and 25 metre DB-5 fused silica WCOT column (J & W Scientific) were employed. GC conditions were: 2 ul sample size; splitless injection mode; injection temperature, 260°C; initial GC temperature 80°C, held for two minutes, programmed at 15°C/min. to 250°C, then at 5°C/min. to 300°C and held for 10 minutes.

The mass spectrometer was operated in the electron impact mode with an electron energy of 32 eV. This value was determined to be optimum for PCDD/PCDF analysis for this instrument from previous work. Selected ion monitoring was used to monitor the characteristic ions for each PCDD/PCDF congener group. For maximum sensitivity, only 6 ions were monitored at any time during the analysis, and 2 or 3 ions were used to monitor each specific PCDD or PCDF congener. Therefore, 5 groups of 6 ions were used to monitor all PCDD and PCDF having 4 or more chlorines. Gas chromatographic separation of the groups of compounds having different numbers of chlorines was sufficient to allow the analysis of these compounds in a single injection for each sample. Nominal masses monitored for the various congeners of PCDD were: tetra, 320 and 322; penta, 354, 356 and 358; hexa, 388, 390 and 392; hepta, 422, 424 and 426; and octa, 458 and 460. For PCDF, the ions were: tetra, 304 and 306; penta, 338, 340 and 342; hexa, 372, 374 and 376; hepta, 406, 408 and 410; and octa, 442 and 444. The previously spiked ^{13}C-2,3,7,8-TCDD was monitored using ions at m/z 332 and 334, and two ions were monitored for ^{13}C-OCDD at masses 470 and 472. The dwell time for each ion was 0.2 seconds. Times for switching groups of ions were determined from injection of a previously analyzed incinerator extract which contained most PCDD and PCDF compounds. The mass analyzer was tuned at the start of each working day using perfluorotributylamine. A single injection detection limit of at least 10 picograms 2,3,7,8-TCDD (S:N 5:1) and at least 20 picograms OCDD (S:N 3:1) was demonstrated before analyzing samples. To be validated as PCDD/PCDF compounds, peaks were subject to the following criteria:

1. peaks must be at least 3 x higher than the average background signal;

2. correspondence of 2 or 3 ions in the known retention time regions for elution of the various congeners;

3. relative peak areas of these ions, normalized to the largest = 100%, must be within 15% of the theoretically correct values;

4. isomer patterns within a specific congener group were used to help identify interferences, since these patterns were very similar for a specific congener, regardless of the type of sample.

2.3.2 Quantification of PCDD/PCDF compounds. To quantify peaks, only one of the masses monitored for each congener group was used (i.e. the mass which gives the largest abundances). The areas of all validated peaks at this mass were determined using a sophisticated data system and compared with standards to determine the amounts of PCDD/PCDF detected. For example, the 322 mass always gives the largest abundance for a TCDD peak, therefore, the areas of all validated TCDD peaks at mass 322 were added together to give the total peak area due to TCDD for a specific sample. This area was converted to total picograms of TCDD by comparing to the area of TCDD from a known standard which was analyzed in a separate injection. This external standard quantification procedure was used for all PCDD/PCDF compounds. All area and concentration calculations were checked at least twice.

The quantification masses used for PCDD compounds were: 322, 356, 390, 424 and 460 for the tetra, penta, hexa, hepta and octachlorinated congeners, respectively. Corresponding masses for PCDF compounds were: 306, 340, 374, 408 and 444. Mass 334 was used to quantify the amount of ^{13}C-2,3,7,8-TCDD spike recovered, and mass 472 was used to quantify ^{13}C-OCDD. Composition of the external standard used for quantification of PCDD/PCDF is shown in Table 1. A relative response factor of 1.0 was assumed for all isomers within a specific congener group. In the case of dibenzofuran congeners for which no standard was available, a relative response factor of 1.0 was assumed between corresponding PCDF and PCDD congeners.

2.3.3 GC analysis and quantification of PCB, CP, CB. Sample extractions for PCB, CP and CB analysis were performed by ORF. Extracts were treated according to the procedures described in Appendix I.

Analysis was performed by gas chromatography using dual capillary column separation with dual electron capture detection. In this method, the injected sample was split onto two columns of different polarity. Each peak has a specific, known retention time that is different for each column. To be identified as a specific compound, a peak must appear at the known retention times for that substance on both columns, and the ratio of the peak areas for the two columns must be the same as the ratio determined from analysis of a standard. When combined with specific clean-up procedures that remove most other components, reliable identifications of specific compounds are obtained. Quantifications were performed by comparing individual compound peak areas to areas of external standards. This method of quantification for PCBs, chlorophenols and chlorobenzenes is a standard procedure that has been in use by M.O.E. for about two years. Occasionally, peak identifications were further confirmed by GC/MS.

TABLE I

COMPOSITION OF EXTERNAL STANDARD

USED TO QUANTIFY PCDD/PCDF

	Congener Name	Abbreviated Name	No. of Chlorines	No. of Isomers	Representative Cpd. in Standard	Conc. in Std. (pg/ul)	Quantification Mass
1.	Tetrachlorodibenzo-p-dioxin	TCDD	4	22	2,3,7,8-TCDD	34	322
2.	Tetrachlorodibenzofuran	TCDF	4	38	2,3,7,8-TCDF	38	306
3.	Pentachlorodibenzo-p-dioxin	P_5CDD	5	14	1,2,3,7,8-P_5CDD	40	356
4.	Pentachlorodibenzofuran	P_5CDF	5	28	quantified versus P_5CDD standard	-	340
5.	Hexachlorodibenzo-p-dioxin	H_6CDD	6	10	1,2,3,4,7,8-H_6CDD	32	390
6.	Hexachlorodibenzofuran	H_6CDF	6	16	quantified versus H_6CDD standard	-	374
7.	Heptachlorodibenzo-p-dioxin	H_7CDD	7	2	1,2,3,4,6,7,8-H_7CDD	42	424
8.	Heptachlorodibenzofuran	H_7CDF	7	4	quantified versus H_7CDD standard	-	408
9.	Octachlorodibenzo-p-dioxin	OCDD	8	1	OCDD	31	460
10.	Octachlorodibenzofuran	OCDF	8	1	OCDF	41	444
Labelled compounds							
11.	^{13}C-2,3,7,8-tetrachlorodibenzo-p-dioxin	^{13}C-2,3,7,8-TCDD	4	-	^{13}C-2,3,7,8-TCDD	30	334
12.	^{13}C-Octachlorodibenzo-p-dioxin	^{13}C-OCDD	8	-	^{13}C-OCDD	35	472

3. RESULTS AND DISCUSSION

3.1 PCDD and PCDF Analysis

Samples from 13 Tests were received for analysis. The final filter weights and volumes of impinger contents for the stack sampling train are listed in Table 2. For each Test, amounts of PCDD/PCDF were determined for stack particulates, impinger contents, two florisil cartridges, feedstock, bottom ash, and precipitator fly-ash. All data were corrected for recoveries of ^{13}C-2,3,7,8-TCDD and ^{13}C-OCDD as described later.

3.1.1 Analysis of stack sampling train. Data from the analysis of stack sampling trains for PCDD/PCDF are presented in Appendix II. These results are reported as total nanograms of each congener detected during the sampling period and, therefore, do not represent concentrations. Since sample collection times were about the same for all Tests, the following qualitative comparisons between Test data can be made.

GC/MS analysis of the various sample types showed some similarities in PCDD/PCDF patterns between different sample types.

Figure 1 is a total ion plot of all PCDD/PCDF compounds detected in the analysis of the Test 4 filter extract. Elution regions of the various congeners are indicated. The pattern shown in Figure 1 is typical of that obtained for filter extracts.

TABLE 2

SUMMARY OF SWARU TESTS PERFORMED

Test	Date Sampled	Impinger Volume (ml)	Particulate Catch (mg)
1	April 21/83	198	194.3
2	Aborted	-	-
3	Aborted	-	-
4	May 4/83	450	44.3
5	May 5/83	490	100.0
6	May 6/83	530	559.3
7	May 10/83	500	64.0
8	May 11/83	500	768.6
9	May 12/83	528	350.9
10	May 13/83	430	122.2
11	May 17/83	492	230.9
12	May 19/83	440	116.6
13	May 24/83	532	176.7
14	May 25/83	440	212.4
15	May 26/83	435	114.3
16	Cancelled	-	-

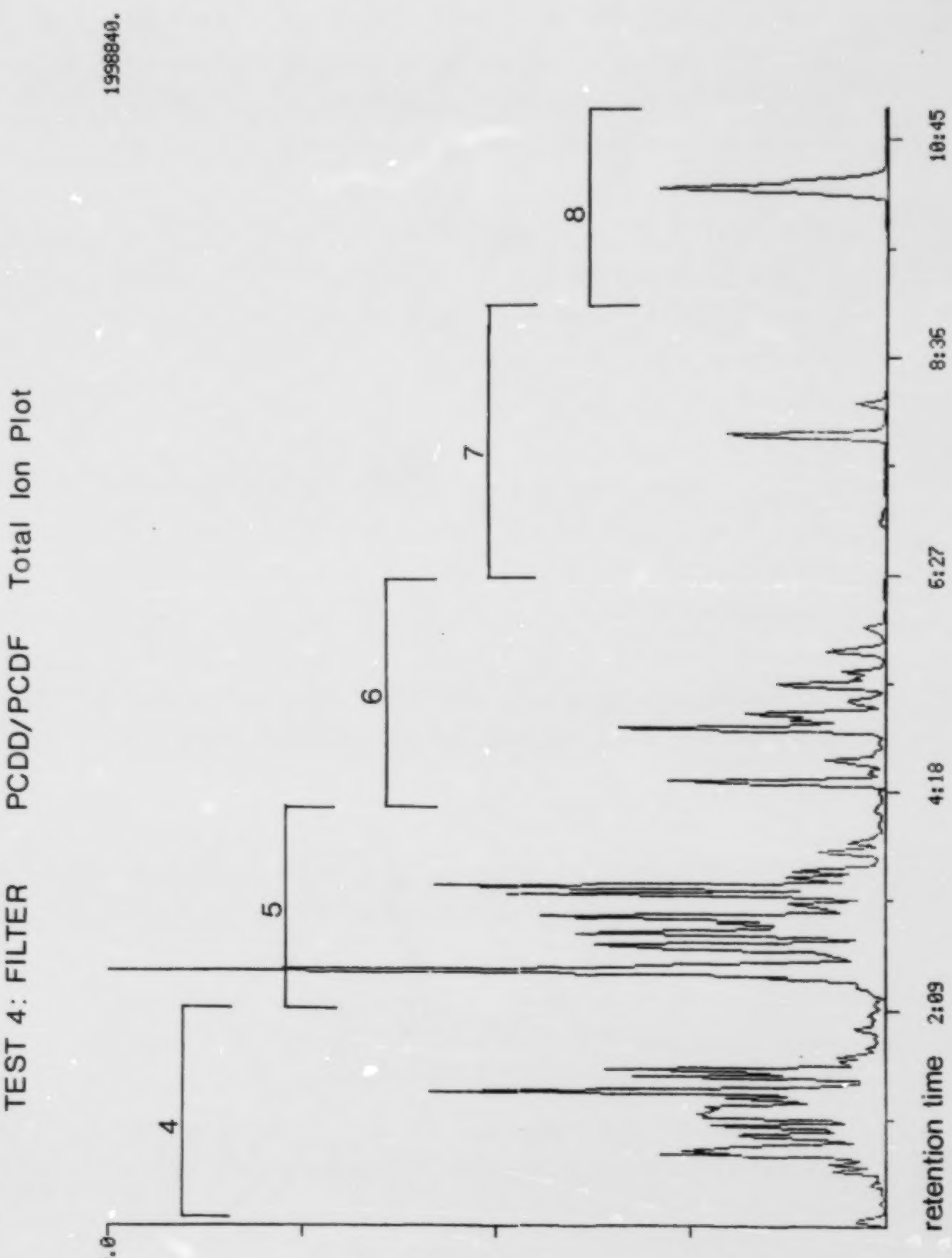

FIGURE 1: PCDD/PCDF Total Ion Plot for Test 4 Filter Analysis

Figure 2 illustrates similarity of patterns between tests by showing the TCDD isomer patterns for the filter, impinger and florisil extracts of Test 4. Corresponding peaks are numbered in the three traces. Although the three traces are similar, minor differences are evident. For example, Peaks 4 and 7 + 8 are more abundant in the filter extract, relative to the other peaks; peak 1 is the largest peak in the impinger and florisil extracts, but not the filter; in some sample extracts, peak 2 was the most abundant. Reasons for these minor differences are not known, but could be from a variety of factors such as volatility differences between isomers or variations in different cleanup columns.

Figure 3 shows that such pattern variations were observed within the same sample type for different Tests. Three H_6CDD analyses are compared for Tests 5, 14 and 15. Peaks 3 and 7 are relatively higher in Test 5 than Test 15, and much lower in Test 14. Peak 2 is much greater than other peaks in Test 14, but only slightly larger than peak 3 in Test 15, and is smaller than peak 3 in Test 5. Such pattern variations as illustrated in Figures 2 and 3 were typical of those observed in all sample extracts.

Because of the combined use of specific clean-up procedures and selective detection, few interfering peaks were detected in the analysis of these incinerator samples for PCDD/PCDF compounds. Occasional artifact peaks were easily identified by only appearing in one of the masses monitored for a specific congener, or by having incorrect ion ratios. Figure 4 illustrates the effectiveness of the analytical procedures for the analysis of pentachlorinated dioxins. Abundances of three ions characteristic of P_5CDD obtained from GC/MS - selected ion monitoring are plotted with respect to retention time. All of the peaks in the m/z 354

TCDD ISOMER PATTERNS
FROM TEST 4 FILTER, IMPINGER, FLORISIL

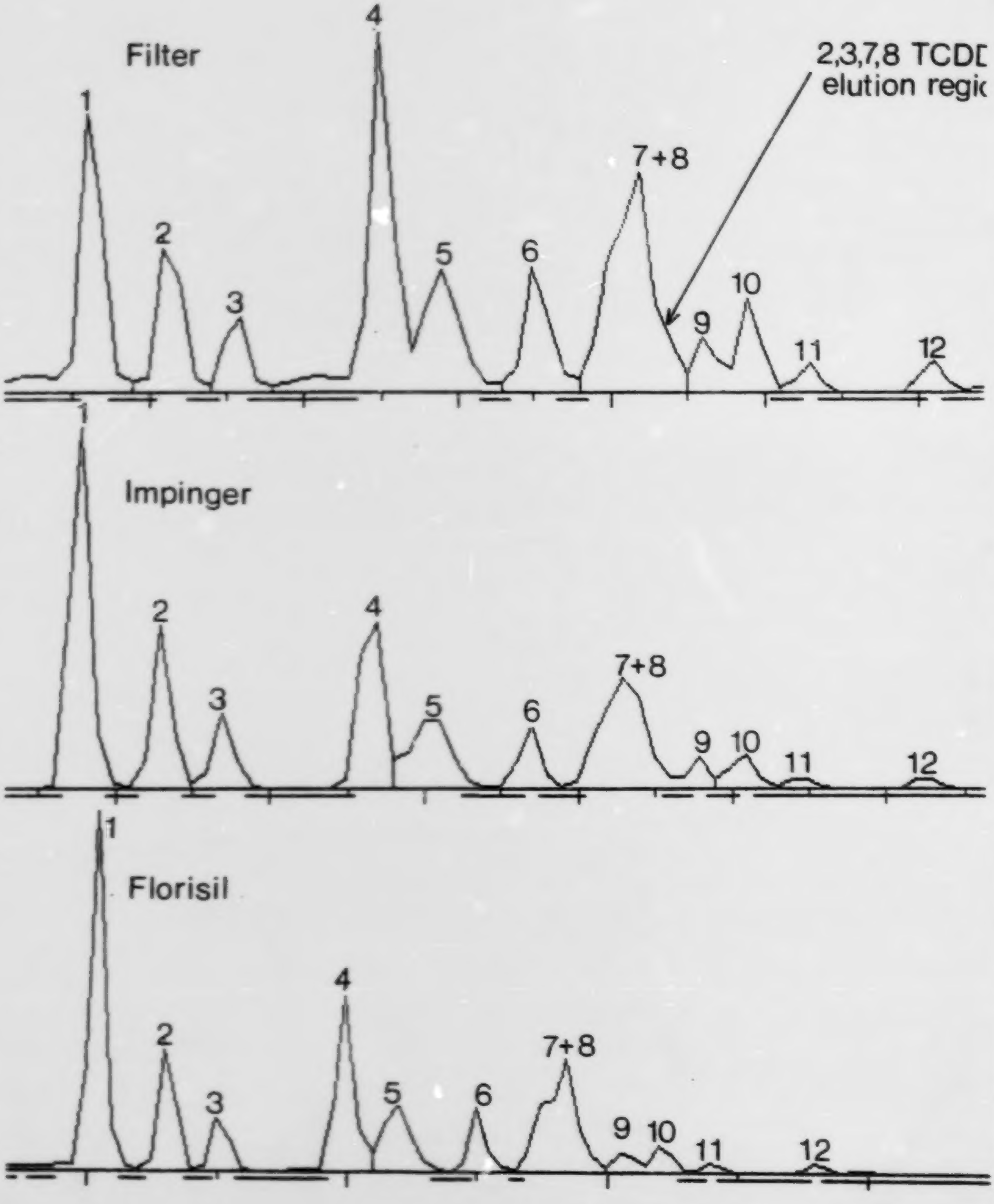

FIGURE 2: TCDD Isomer Patterns for Analysis of Test 4 train extracts

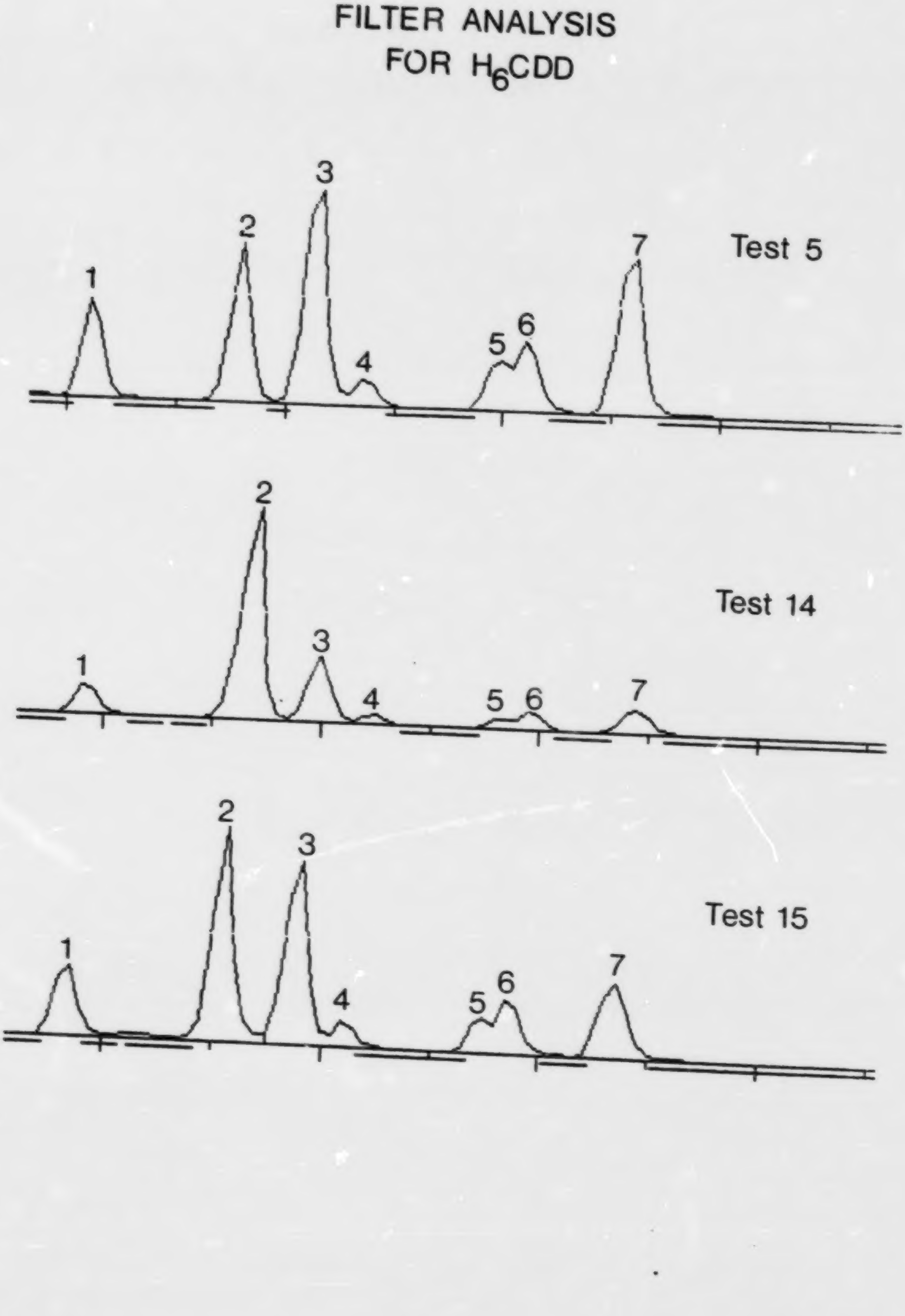

FIGURE 3: Analysis of Filter Extracts for H_6CDD

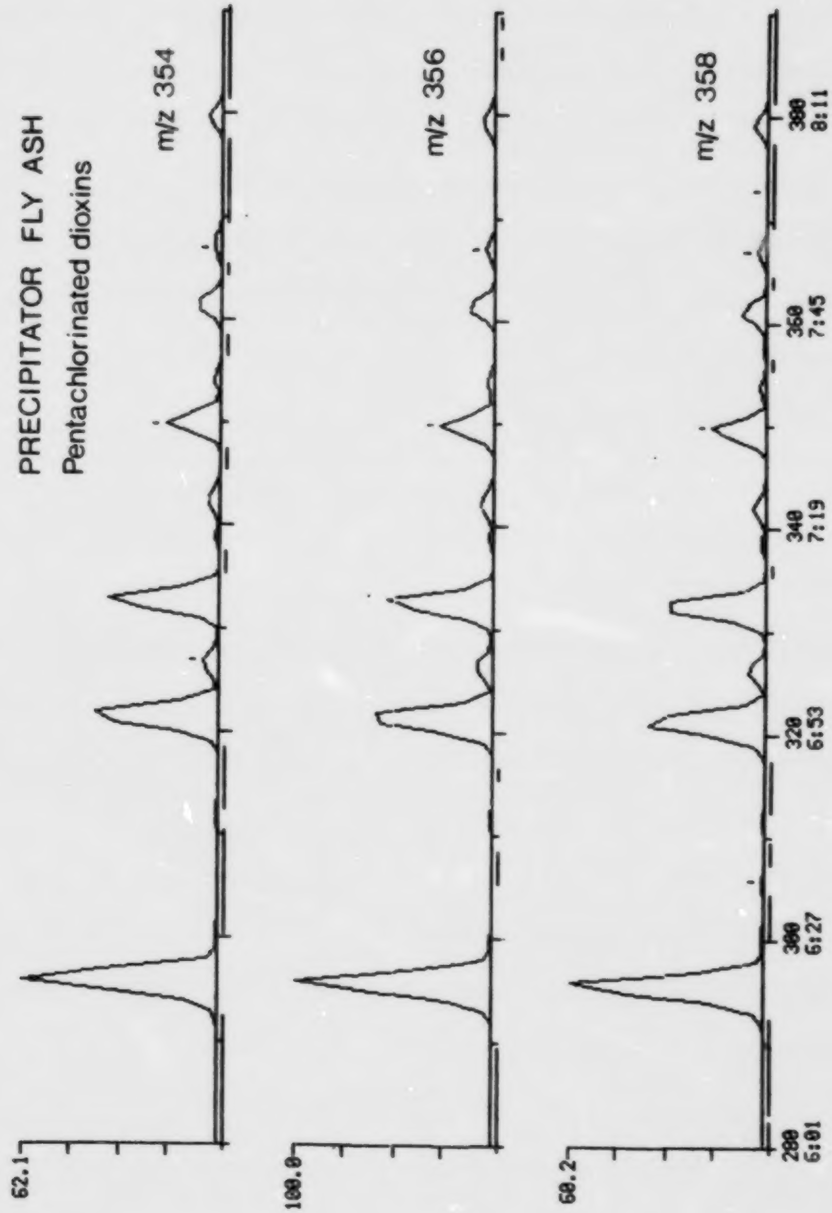

FIGURE 4: Plot of Characteristic Ions for Analysis of P_5CDD in an Incinerator Sample Extract

trace have corresponding peaks in the m/z and m/z 358 traces. Also, the 354:356:358 abundance ratios of peaks in figure 4 are 62: 100: 60, which are almost identical to the P_5CDD theoretical ratios of 61:100:65.

The terms of reference for this study did not require isomer-specific analysis of 2,3,7,8-TCDD, since the Provisional Guideline is for total PCDD and PCDF. Because the ^{13}C-2,3,7,8-TCDD internal standard was present in all sample extracts, the retention time of native 2,3,7,8-TCDD can be specified accurately on the plots shown in Figure 2. If present, native 2,3,7,8-TCDD would elute on the shoulder of peak 8, as indicated. From approximate peak heights, this could only account for 0 to 5%, maximum, of the total TCDD in these samples.

3.1.2 Summary of train data. Table 3 is a summary of the PCDD/PCDF train data in Appendix II. On average, the total PCDD/PCDF amounts were divided almost equally between filters and impingers. Total contribution of the florisil cartridges was only about 7% of the total PCDD/PCDF amounts in the entire train. The average total PCDD/PCDF for 13 Tests is 16500 nanograms, proportioned as 30% PCDD and 70% PCDF compounds. It does not necessarily follow that different Tests should have the same relative distribution of PCDD/PCDF compounds or the same total amounts because the Tests are different controlled experiments in which some Test conditions were varied.

Average relative congener distributions of PCDD/PCDF for 13 Tests are shown in Table 4. As previously stated, data have not been corrected for stack gas volume sampled, and results shown in Table 4 represent general trends in the train data. For comparison purposes, the average congener distributions of fly-ash are also included.

TABLE 3

SUMMARY OF PCDD/PCDF IN TRAIN SAMPLES *

Total Nanograms in Train Components

TEST	FILTER+			IMPINGER			FLORISIL**			TRAIN TOTAL		
	PCDD	PCDF	Total	PCDD	PCDF	Total	PCDD	PCDF	Total	PCDD	PCDF	Total
1	2800	7800	11000	1600	7700	9300	230	1100	1300	4600	16000	21000
4	770	760	1500	2300	3600	5900	370	520	900	3400	5000	8400
5	2200	4900	7100	3900	14000	18000	340	1300	1600	6400	21000	27000
6	8600	19000	28000	720	1700	2400	85	180	270	9400	21000	30000
7	3600	8500	12000	1400	6500	7900	150	440	590	5200	16000	21000
8	1000	2300	3300	820	2900	3700	340	1400	1700	2200	6700	8900
9	2900	9400	12000	190	1200	1400	42	270	310	3100	11000	14000
10	720	900	1600	2000	3800	5800	810	2000	2800	3500	6500	10000
11	1700	6000	7700	510	2500	3000	270	620	890	2500	9500	12000
12	560	580	1100	3800	7400	11000	460	1000	1500	4800	9200	14000
13	1800	7000	8800	440	2300	2700	170	930	1100	2400	11000	13000
14	4200	5200	9400	5000	5200	10000	180	210	390	9400	11000	20000
15	940	920	1900	4700	7500	12000	290	540	830	5900	9100	15000
Average	2400	5600	8100	2100	5100	7200	290	810	1100	4800	11700	16500
Std. Dev.	2200	5000	7300	1700	3500	4800	200	540	700	2400	5200	6800

***All values corrected for recovery but not for volume of stack gas sampled**

+Values for 1st extraction only

****Total of both cartridges**

TABLE 4

AVERAGE PCDD/PCDF CONGENER DISTRIBUTIONS

(Normalized to Most Abundant PCDD or PCDF Congener = 100)

CONGENER		FILTER	IMPINGER	FLORISIL	FLY-ASH
A. Dioxins	TCDD	100	100	100	40
	P_5CDD	100	90	90	70
	H_6CDD	100	90	60	100
	H_7CDD	50	30	40	30
	OCDD	40	20	10	20
Avg. Total Nanograms		2400	2100	290	-
B. Furans	TCDF	100	100	100	70
	P_5CDF	90	90	60	100
	H_6CDF	40	40	20	80
	H_7CDF	10	6	3	20
	OCDF	3	2	1	2
Avg. Total Nanograms		5600	5100	810	-

The total PCDD amounts are composed of a greater proportion of the higher chlorinated congeners than are total PCDF amounts, although average relative congener distributions for both PCDD and PCDF follow the same pattern in most train sample extracts. Tetra and penta congeners are most abundant, and increasingly lower amounts are present for each higher degree of chlorination. Fly-ash has a lower relative concentration of the tetrachlorinated congeners, highest relative concentration of the penta (furans) or hexa (dioxins) chlorinated congeners, and stepwise decreasing relative concentrations of the higher chlorinated congeners. The octachlorinated congeners in fly-ash have the lowest relative abundances.

3.1.3 PCDD/PCDF in Florisil Cartridges. A dual florisil cartridge design was incorporated into the stack sampling train so that the efficiency of the impinger - single florisil cartridge design could be monitored. If the collection efficiency of the florisil cartridge was ideal, it would be expected to trap all PCDD/PCDF in the first cartridge, until the saturation level for that cartridge was reached. The second cartridge would then serve as back-up, to trap the remaining PCDD/PCDF. From the florisil data presented in Appendix II, it is observed that except for Test 9, some PCDD/PCDF always reaches the second florisil trap. This was the case even for Test 6 in which the amount trapped on the first cartridge was the lowest of any Test. These data may reflect differences in the efficiency of preparing the florisil traps. In about one-half of the Tests, the amounts collected in the first cartridge were in a narrow range of 1100 to 1700 nanograms, and this may represent the capacity of a well-prepared cartridge under the given experimental conditions. For Tests 10 and 11, the amounts detected in the second florisil trap were higher than in the first trap. In Test 10, this may be a result of the capacity of the first trap being exceeded, since 1100 ng were detected on it. This could not be the case in Test 11, where only 350 ng were detected on the initial florisil cartridge. In this case, another effect such as inefficient packing of this cartridge could cause the observed results. Because of the two-trap system, however, the fraction of organic compounds in the sampled stack emissions that is not trapped is minimized.

Table 5 compares the quantities of PCDD/PCDF detected in the florisil traps with amounts collected in the impinger and the total train. On average, the florisil traps contained 7% of the total PCDD/PCDF detected in the train and 14% of the total amount excluding the quantity detected in the filter extracts. The second florisil trap collected only 0.3% of the total PCDD/PCDF in the entire train, and 5% of the total detected in both florisil traps. While these results indicate that the collection efficiency of the filter, impingers and first florisil trap is high, Tests 10 and 11 show that the second florisil trap was necessary. A dual adsorbent trap system provides increased confidence in collecting all PCDD/PCDF in the stack gases sampled. Because the average amount detected in the second florisil trap was only 0.3% of the total PCDD/PCDF found in the entire train, the amount of PCDD/PCDF which is not collected by the stack sampling system can be assumed to be negligible.

3.1.4 Comparison of 1st and 2nd Filter Extractions.

In previous incinerator work 48 hour Soxhlet extraction periods were employed for particulate samples such as filtered stack particles and precipitator fly-ash. This extraction period was reduced to 16 hours for this study, and to

TABLE 5

COMPARISON OF PCDD/PCDF IN FLORISIL TRAPS* WITH IMPINGER AND TOTAL TRAIN

TEST	TOTAL in TRAIN	% of TOTAL in F1 + F2	% of VAPOUR** COMPONENT in F1 + F2	% of TOTAL in F2	% of F1 + F2 in F2
1	21000	6	13	0.4	6
4	8400	11	13	0.5	5
5	27000	6	8	0.4	7
6	30000	1	10	0.1	9
7	21000	3	7	0.3	9
8	8900	19	33	1.1	5
9	14000	2	22	0	0
10	10000	28	33	17	61
11	12000	7	23	4.4	60
12	14000	11	12	0.6	6
13	13000	9	29	0.1	1
14	20000	2	4	0.1	1
15	15000	6	6	0.2	4
Average +	17000	7	14	0.3	5
Std. Dev.	7000	5	10	0.3	3

*F1 = First Florisil Trap; F2 = second Florisil Trap

**Vapour Component = Total Nanograms in Impingers + Total Nanograms in both Florisil Traps

+TEST 10 and TEST 11 not included

check extraction efficiency a second 16-hour Soxhlet extraction of the filters was performed and these extractions treated as separate samples. Table 6 is a comparison of the total PCDD/PCDF amounts detected in the 2nd 16-hour extractions with the total PCDD/PCDF in the sampling trains and with the amounts detected in the initial 16-hour extraction. An average of only 0.63% of the total train PCDD/PCDF was found in the second filter extract. This includes the Test 11 value of 4.17% which is more than 3 standard deviations greater than the overall mean. Omitting this value, the overall mean is 0.33%. The average PCDD/PCDF in the second filter extract was 1.18% of the amount detected in the first 16-hour extraction, or 0.74% if Test 11 is omitted. These data show that a single 16-hour extraction period is sufficient to remove about 98% of the extractable PCDD/PCDF compounds from the filtered particulate material collected by the stack sampling train. Also, almost 100% of the spiked ^{13}C-TCDD and ^{13}C-OCDD were recovered in the first 16-hour extraction.Since this finding is based on a comparison of within-train amounts, it is independent of the specific stack gas volumes sampled in the various Tests.

3.1.5 Analysis of process samples

Data for the analysis of feedstock, bottom ash, and precipitator fly-ash are presented in Appendix II. Extracts of feedstock samples contained such high loadings of organic compounds that it was necessary for them to undergo treatment by the clean-up columns a second time. This accounts for the lower average spike recoveries for feedstock samples compared to other sample types.

TABLE 6

COMPARISON OF PCDD/PCDF IN 2ND FILTER EXTRACTION WITH 1ST FILTER EXTRACT AND TOTAL TRAIN*

TEST	TOTAL ng IN TRAIN	% of TOTAL TRAIN ng IN 2nd FILTER EXTRACT	2nd FILTER EXTRACT % of 1st FILTER EXTRACT
1	21000	0.41	0.78
4	8400	0.01	0.05
5	27000	0.59	2.25
6	30000	1.33	1.48
7	21000	0.32	0.56
8	8900	0.16	0.41
9	14000	0.12	0.14
10	10000	0.10	0.63
11	12000	4.17	6.49
12	14000	0.03	0.44
13	13000	0.03	0.04
14	20000	0.85	1.79
15	15000	0.04	0.34
Average	17000	0.63	1.18
Std. Dev.	7000	1.1	1.74

*2nd 16-hour extractions of filter not corrected for recovery; all other results are corrected for recovery

All feedstock extracts contained low concentrations of H_7CDD and OCDD, but few of the other PCDD/PCDF congeners were detected. Concentrations of PCDD/PCDF in combined ash were also very low, and two of the Tests (4 and 5) contained no detectable levels of the chlorinated dioxins or furans analyzed. Concentration of PCDD/PCDF in the precipitator fly-ash were lower than have often been reported for this type of sample by others for fly-ash taken from other municipal incinerators, where total PCDD/PCDF concentrations can be several hundreds of nanograms per gram of fly-ash extracted. In this work, the average total chlorinated dioxins and furans in fly-ash for 13 Tests was 69 (S.D. 48) ng/g. Table 7 is a summary of the process sample analyses.

Isomer patterns within the various PCDD/PCDF congeners were not the same for feedstock and bottom ash extracts as for the extracts from filter, impinger and florisil components of the sampling train. For bottom ash, the levels of PCDD/PCDF were so low that for most samples, only a few of the most abundant isomers of a congener group could be detected. For Test 1 and Test 14 (bottom ash) the number of isomers observed and isomer patterns for each specific congener grouping was similar to the number and patterns usually detected in the fly-ash, impinger, and filter samples analyzed in this study.

For feedstock extracts, this was not the case, as almost all of the total PCDD/PCDF detected were chlorinated dioxin compounds. Chlorinated furans were only detected in feedstock extracts for Tests 1, 3, and 14. Table 8 shows the percentages of total nanograms PCDD + PCDF compounds detected which were chlorinated dioxins. The train sample extracts and fly-ash extracts showed a general distribution of about 70:30 for amounts detected of PCDF/PCDD compounds. However, over 90% of these compounds detected in the feedstock extracts were chlorinated dioxins. Furthermore, almost all of the PCDD detected was from the two H_7CDD isomers and from OCDD.

TABLE 7

SUMMARY OF ANALYTICAL DATA * FOR PCDD/PCDF IN PROCESS SAMPLES

	FEEDSTOCK			BOTTOM ASH			PRECIPITATOR FLY-ASH		
TEST	PCDD	PCDF	PCDD+PCDF	PCDD	PCDF	PCDD+PCDF	PCDD	PCDF	PCDD+PCDF
1	8.8	25	34	0.6	1.1	1.7	33	87	120
4	10	ND	10	ND	ND	ND	94	110	200
5	4.0	4.0	8.0	ND	ND	ND	33	67	100
6	3.7	ND	3.7	-	-	-	11	31	42
7	13	ND	13	ND	1.3	1.3	14	54	68
8	6.5	ND	6.5	0.7	ND	0.7	9.5	48	58
9	12	ND	12	0.4	0.4	0.8	7.7	24	32
10	17	ND	17	0.1	ND	0.1	17	29	46
11	16	ND	16	0.1	ND	0.1	9.6	35	45
12	10	ND	10	0.5	ND	0.5	17	22	39
13	97	ND	97	0.1	ND	0.1	11	32	43
14	29	1.3	30	3.3	3.9	7.2	35	41	76
15	30	ND	30	0.4	ND	0.4	6.2	23	29

* All results in ng/g

All data are corrected for recoveries

TABLE 8

PERCENT PCDD DETECTED IN INCINERATOR EXTRACTS*

TEST	TRAIN				FLY ASH	FEEDSTOCK
	Filter	Impinger	Florisil	Total		
1	25	18	17	22	27	26
4	51	39	41	42	47	100
5	31	22	21	24	33	50
6	32	30	33	32	27	100
7	31	18	26	25	21	100
8	30	22	19	25	16	100
9	24	14	14	22	24	100
10	45	35	29	35	38	100
11	22	17	30	22	21	100
12	50	35	31	34	43	100
13	20	16	15	18	25	100
14	44	50	46	47	46	99
15	50	39	35	39	21	100
Average	35	27	27	30	30	90
Std. Dev.	11	11	10	9	10	24

*Numbers are % nanograms PCDD of total nanograms PCDD + PCDF detected

3.1.6 Spiking of samples and recovery correction. As a quality control procedure for all PCDD/PCDF analyses, samples were spiked with known amounts of ^{13}C-labelled TCDD and ^{13}C-labelled OCDD before extraction. Spiking levels were chosen to be close to expected levels of native PCDD/PCDF compounds. These spiked compounds can be monitored during the same analysis as native PCDD/PCDF compounds because they will be detected at different masses than native TCDD or OCDD. However, the chemical behaviour of the labelled compounds will be the same through the extraction, clean-up and instrumental analysis as the native compounds. Therefore, losses of native compounds through these operations are compensated by correcting results according to recoveries of the labelled TCDD and OCDD. The amounts of the labelled compounds detected are determined by external standards using the same procedures as the native compounds. For example, if 10 ng of ^{13}C-TCDD were added to a sample before extraction, but only 5 ng were detected later by GC/MS analysis, then the recovery is 50% and the total native TCDD amount would be adjusted accordingly. Ideally, a separate labelled compound representative of each PCDD/PCDF congener would be spiked onto each sample. However, only ^{13}C-TCDD and ^{13}C-OCDD were available for this study. Levels of TCDD, TCDF, P_5CDD, P_5CDF, H_6CDD and H_6CDF were corrected for the ^{13}C-TCDD spike recovery, while H_7CDD, H_7CDF, OCDD and OCDF were corrected for the ^{13}C-OCDD spike recovery. The technique of recovery correction is an accepted analytical procedure in organic trace analysis.

Recovery correction adjusts for sample losses during extraction and clean-up, instrumental variation, and sample storage effects such as evaporation of solvent during storage. However, the correction is for all of these factors, and the amount of correction that can be attributed to a specific source of variation such as recovery from extraction is indeterminable in this study. Duplicate injections of the filter and impinger samples for this study were performed and although the spike recoveries sometimes varied greatly between duplicate injections of the same sample, results were very close after adjustment for spike recoveries. Because recovery variations include instrumental and sample storage effects, reported recoveries can be greater than 100%.

3.1.7 Comparison of recovery data. Average recoveries of ^{13}C-2,3,7,8-TCDD and ^{13}C-OCDD, which were spiked onto samples before extraction, are shown in Table 9. For train samples, average TCDD recoveries were 54%, 72% and 56% for filter, impinger, and florisil samples extracts, respectively. Corresponding values for OCDD were: 39%, 50% and 31%. Differences in recoveries for the various types of samples are expected, primarily because of the different extraction procedures employed. Also, OCDD is more difficult to extract than TCDD, and this is reflected in the lower recoveries shown in Table 9. Average feedstock recoveries are low because these samples were put through column clean-up twice. Bottom ash and fly-ash recoveries are variable and generally high. Values greater than 100% are not unexpected, and can result from normal variations in the analysis procedure. However, recoveries greater than 120% are of special concern, since they indicate a problem with the quantification procedure, spiking procedure, or unknown sample matrix effects. Fly-ash samples were extracted a second time, and spike recoveries were comparable to the spike recoveries obtained for the initial extraction.

Furthermore, the samples with highest recoveries for the first extraction also had the highest recoveries for the second extraction. This indicates that sample matrix effects could be present, although no interfering compounds for the ^{13}C-2,3,7,8-TCDD or ^{13}C-OCDD internal standards have been detected. Fly-ash samples were the only ones in which the average OCDD recovery was higher than the average TCDD recovery.

3.2 PCB, Chlorophenol and Chlorobenzene Analysis

Extractions of train and process samples for polychlorinated biphenyls (PCB), chlorinated phenols (CP) and chlorobenzene (CB) compounds were performed by ORF personnel. Extracts were cleaned-up as described in Appendix I and analyzed by gas chromatography - electron capture detection (GC-ECD). Quantifications were based on comparison of GC peak areas with those of external standards.

PCB, CP, and CB data for train and process samples are tabulated in Appendix II. For determination of stack emissions, extracts of the filter, impingers and florisil cartridges for each sampling train were combined and analyzed as a single sample. Therefore, only total stack emissions for PCB, CP and CB are presented in the Appendix. Average amounts detected in the stack emissions were 8500 ng, 920 ng, and 200,000 ng for CB, PCB, and CP, respectively. As was stated for the average PCDD/PCDF values reported earlier, these values are only generally comparable since they have not been corrected for the volume of stack gases sampled.

PCB levels are very low, and are less than 0.5%, on average, of the total CB and CP detected in the stack emissions. No significant correlation, based on linear regression analysis, exists between levels of PCB and CB or CP in the stack sample extracts.

Amounts of PCB for most Tests were about the same per gram of feedstock as for the total stack emissions sampled. Average levels were much higher in the feedstock because of very high amounts detected in Tests 5 and 13, compared to the rest of the Tests. Chlorobenzene concentrations were very low in all process samples. Chlorophenol concentrations were very low in the bottom ash and precipitator fly-ash extracts, but much higher in feedstock extracts. Generally, concentrations of PCB, CB and CP compounds were much higher in the feedstock than in the other process samples. Bottom ash contained insignificant levels of these substances compared to the feedstock and fly-ash, while average concentrations in fly-ash were about 3 to 10 times lower than in feedstock.

3.3 Error Analysis

Determination of the variance in the total analysis method, which includes stack sampling, extraction, sample clean-up and GC or GC/MS analysis, requires simultaneous stack sampling with multiple trains.

TABLE 9

COMPARISON OF RECOVERY DATA FOR PCDD/PCDF ANALYSIS OF INCINERATOR SAMPLE EXTRACTS*

TEST	FILTER		IMPINGER		FLORISIL+		FEEDSTOCK		BOTTOM ASH		FLY-ASH	
	TCDD	OCDD	TCDD	OCDD	TCDD	OCDD	TCDD	OCDD	TCDD	OCDD	TCDD	OCDD
1	35	29	72	72	45	24	4	11	45	43	190	130
4	53	50	74	59	80	11	10	11	330	26	170	390
5	110	94	31	16	25	35	29	34	39	76	150	1000
6	17	27	76	25	50	39	30	55	-	-	260	330
7	57	52	110	83	52	40	28	56	16	65	330	590
8	95	36	63	150	55	43	22	33	130	220	51	120
9	41	37	96	85	44	8	25	45	270	116	86	60
10	48	27	30	16	74	12	16	8	75	13	97	150
11	27	11	112	43	44	20	22	16	72	51	98	160
12	60	25	55	48	85	24	7	7	260	103	130	150
13	41	30	45	26	58	81	1	3	130	71	120	130
14	63	70	124	12	53	44	14	14	72	9	72	77
15	59	28	49	20	69	25	12	10	98	48	59	42
Average	54	39	72	50	56	31	17	23	130	70	140**	190**
Std. Dev.	26	23	31	40	17	19	10	19	100	57	85	160

*TCDD = % recovery of ^{13}C-2,3,7,8-TCDD added before extraction

OCDD = % recovery of ^{13}C-OCDD added before extraction

+Recoveries from first florisil cartridge

**Average does not include Test 5 values

Parallel sample processing and analysis of such replicates would give a true measure of the overall reproducibility of the procedures described in this report. However, such an experiment has not been conducted for this study. Furthermore, no such study has yet been reported by any other group involved in stack sampling for PCDD/PCDF. Although the total overall analytical variance is therefore unknown in this study, some components of this variance have been determined and can be used as an estimate of the lowest possible variance.

3.3.1 Discussion of error - PCDD and PCDF. Principal sources of analytical variance are as follows:

(a) sampling of stack gases and particulates;

(b) recovery of sample from train;

(c) spiking of train and process samples with ^{13}C-2,3,7,8-TCDD and ^{13}C-OCDD as internal standards;

(d) extraction of samples;

(e) sample clean-up;

(f) concentration of sample to final volume for analysis;

(g) storage effects such as adsorption onto glass walls of storage container, decomposition, and concentration from solvent evaporation; and

(h) instrumental and quantification variation.

(a) Variation in sampling procedures cannot be quantified accurately for this work, since duplicate train and process samples were not collected. Because the stack sampling procedures were designed to minimize the effects of inhomogeneity in the stack emissions, it is assumed that the collected sample is representative of these emissions. The same assumption is made for process samples. More variability may exist in the feedstock analyses, since sampling of bulk materials required manual sorting of inhomogenous materials. The efficiency of the sampling trains was very high, because the average PCDD/PCDF amount collected on the second florisil cartridge was 0.5% of the total collected by the train.

(b) Recovery of PCDD/PCDF from the train should not contribute to the overall analytical variance. Multiple glassware rinsing using solvents of various polarity is an effective method of sample recovery, especially for this study in which levels of PCDD/PCDF in the sampling trains were high. Any PCDD/PCDF not removed from the train should be insignificant compared to the large amounts that were recovered.

(c,d,e) Spiking of samples with labelled TCDD and OCDD, extraction, and sample clean-up all contribute to the analytical variance. Recovery corrections will correct, in part, for losses in the extraction and clean-up steps. The variance that can be attributed to each of these procedures separately cannot be determined in this study. Since duplicate samples were not available, the combined variance also cannot be determined. From previous work, the relative reproducibility in column clean-up is about 5%. No separate estimate of extraction reproducibility is available, although this contribution to the total should be low after recovery correction. Some bias in correcting for penta-hexa - and hepta - congeners could exist because only ^{13}C-TCDD and ^{13}C-OCDD were used as internal standards. Since the predominant congeners were the tetrachlorinated and pentachlorinated, however, such bias if present should have little effect on the determination of totals. Also, the penta and tetrachlorinated congeners behave similarly in terms of the clean-up procedures and in GC-MS response factors.

(f, g) Concentrated sample extracts were stored in reacti-vials equipped with screw-caps and teflon liners in a freezer at about -5°C until analysis. At this reduced temperature and stored away from sources of light, PCDD and PCDF stability is not a problem, even for extended periods of storage. Adsorption effects are also not expected to be significant, since care was taken to prevent the evaporation of solvents to dryness. Any effects due to solvent evaporation and PCDD/PCDF adsorption will be corrected for by adjusting the analytical results for recoveries of the labelled compounds added before extraction.

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(h) Instrumental and quantification variations were determined by multiple injections of sample extracts. Table 10 is a comparison between original and reinjected analyses for three SWARU impinger samples, after spike correction. Ideally, original and reinjected amounts should be identical after correcting for spike recovery. Differences in replicate injections are indicative of all variations in analytical reproducibility after the sample clean-up stage. This includes injection procedures, instrumental variation, and sample storage effects. From Table 10, an estimate of the percent relative errors for various PCDD and PCDF congeners can be obtained. For a specific value, its percent relative error is taken to be the percent difference of that value from the average of the replicate injections.

Generally, the TCDD, TCDF, P_5CDD and P_5CDF congeners behave similarly in terms of standard response factors. The average percent deviations for these congeners from Table 10 is 7%. For the H_6CDD and H_6CDF congeners, this value is 16% and for H_7CDD, H_7CDF, OCDD and OCDF congeners, 18%. Although the average individual congener variations were as stated above, the accuracy of the total PCDD/PCDF is 5%. This is because the highest contribution to the total PCDD/PCDF values are the tetra and penta congeners, which have the highest accuracy and reproducibility, and because random variations for individual congeners have a reduced effect on the determination of totals.

TABLE 10

COMPARISON OF REPLICATE ANALYSIS OF IMPINGER EXTRACTS**

(ng in total sample)

CONGENER	TEST 8				TEST 11				TEST 13			
	I	II	Aver.	% dev.*	I	II	Aver.	% dev.*	I	II	Aver.	% dev.*
TCDD	400	270	335	19	200	200	200	0	170	200	185	8
TCDF	1700	1400	1550	10	1400	1500	1450	3	1000	1100	1050	5
P_5CDD	170	180	175	3	210	180	195	8	150	140	145	3
P_5CDF	860	930	895	4	880	1200	1040	15	1000	920	960	4
H_6CDD	170	98	134	27	79	77	78	1	110	58	84	31
H_6CDF	330	270	300	10	210	360	285	26	290	290	290	0
H_7CDD	54	46	50	8	16	14	15	7	8.1	15	12	30
H_7CDF	13	10	12	13	14	4.3	9.1	31	3.1	5.2	4.1	25
OCDD	30	31	31	2	6.3	5.3	5.8	9	3.1	3.3	3.2	3
OCDF	9.3	6.6	8	17	0.7	1.1	0.9	22	0.4	1.0	0.7	43
TOTAL	3740	3240	3490	7	3020	3540	3280	8	2730	2730	2730	0
Recoveries												
-TCDD (%)	63	94	79	20	110	130	120	7	45	72	59	23
-OCDD (%)	150	35	58	40	43	65	54	20	26	21	24	11

**all values corrected for recovery

*%dev. = percent difference of analysis I or II from average

3.3.2 Discussion of Error - PCB, CP, CB. Because the technique of gas chromatography cannot distinguish between native and labelled compounds, samples for PCB, CP, CB were not spiked before extraction and results were not adjusted for recoveries. In a previous study, blanks were spiked with standards and processed through the extraction, clean-up, and GC analysis to estimate typical recoveries. Table 11 summarizes these data. The average recoveries were very consistent for individual species within a specific class of compounds. Overall average percent recoveries were 92 4 for PCB, 76 9 for polychlorinated phenols, and 93 4 for polychlorinated benzenes. The data in Table 11 show that very consistent results can be achieved for PCB, chlorophenol and chlorobenzene determinations. Since samples were extracted by personnel of the Ontario Research Foundation, and the data from Table 11 were from M.O.E. analysis of blanks only, it cannot be determined whether Table 11 represents the recoveries achieved for actual samples. Therefore, recovery corrections were not applied for PCB, chlorophenol and chlorobenzene data in Appendix II.

As a measure of the instrumental error, standard mixtures of chlorophenols and chlorobenzenes were analyzed 6 times by the dual capillary column GC method described previously. Table 12 shows the results of this study. Average percent relative standard deviations were 2.6 for chlorophenols and 1.5 for chlorobenzenes. These values are representative of the average errors associated with the instrumental analysis, and do not include variations due to sampling or extraction and cleanup procedures. However, the total variation due to all procedures after sampling should be about the same as the average variations of the spike recoveries from blanks that are presented in Table 11. Average variations of results from multiple determinations of PCB standards were not determined.

TABLE 11

RECOVERIES OF SPIKED COMPOUNDS FROM ANALYSIS OF BLANKS FOR PCBs, CHLOROPHENOLS, CHLOROBENZENES

COMPOUND	NUMBER OF DETERMINATIONS	SPIKING LEVEL	MEAN RECOVERY (%)	STANDARD DEVIATION
A. Polychlorinated Biphenyls				
1. PCB Mix	13	3000 ng/ml (total)	92	3.8
B. Polychlorinated Phenols				
1. 2,4,6-Tri	15	500 ng	75	9.4
2. 2,4,5-Tri	15	2000 ng	75	9.0
3. 2,3,4-Tri	15	1000 ng	75	9.5
4. 2,3,5,6-Tetra	15	500 ng	77	8.2
5. 2,3,4,5-Tetra	15	500 ng	79	7.3
6. Penta	15	500 ng	77	8.5
C. Polychlorinated Benzenes				
1. 1,3,5-Tri	13	100 ng	91	4.6
2. 1,2,4-Tri	13	100 ng	92	5.1
3. 1,2,3-Tri	13	100 ng	92	5.7
4. 1,2,4,5-Tetra	13	100 ng	92	4.6
5. 1,2,3,5-Tetra	13	100 ng	92	3.2
6. 1,2,3,4-Tetra	13	100 ng	94	3.8
7. Penta	13	100 ng	94	3.4
8. Hexa	13	100 ng	95	4.2

TABLE 12

ANALYTICAL REPRODUCIBILITY FOR ANALYSIS OF CHLOROPHENOLS AND CHLOROBENZENES*

COMPOUND	CONCENTRATION OF STD (nanograms)	STANDARD DEVIATION	PERCENT RELATIVE STANDARD DEVIATION
A. Chlorinated Phenols			
1. 2,3-Di	50	0.7	1.4
2. 2,6-Di	50	1.1	2.2
3. 3,5-Di	50	0.3	0.7
4. 2,5-Di	50	0.9	1.9
5. 2,4-Di	50	0.7	1.4
6. 2,4,6-Tri	20	0.5	2.5
7. 2,3,6-Tri	20	0.5	2.4
8. 2,4,5-Tri	20	0.3	1.6
9. 2,3,5-Tri	20	0.7	3.8
10. 2,3,4-Tri	20	0.6	3.1
11. 2,3,5,6-Tetra	20	0.7	3.5
12. 2,3,4,6-Tetra	20	0.9	4.9
13. 2,3,4,5-Tetra	20	0.6	3.0
14. Penta	20	0.8	4.0
B. Chlorinated Benzenes			
1. 1,3,5-Tri	10	0.1	1.2
2. 1,2,4-Tri	10	0.2	1.6
3. 1,2,3-Tri	10	0.2	1.5
4. 1,2,4,5-Tetra	10	0.2	1.8
5. 1,2,3,5-Tetra	10	0.1	1.0
6. 1,2,3,4-Tetra	10	0.1	1.2
7. Penta	10	0.2	2.0
8. Hexa	10	0.1	1.4

* Based on six injections of each component.

APPENDIX I

LABORATORY CLEAN-UP OF INCINERATOR SAMPLE EXTRACTS FOR PCDD/PCDF

Clean-up:	Ref:	T. J. Nestrick
		L. L. Lamparski
		Anal. Chem. 51 1979

PREPARATION OF ADSORBENTS

I. 44% Sulfuric Acid on Silica. Chromatographic grade silicic acid as 100/200 mesh Bio-Sil A is initially dried in a glass tube furnace for about 30 minutes at 180°C under a continuous dry nitrogen purge. It is then removed from the furnace and cooled to ambient temperature, and subsequently rinsed with consecutive 100 ml portions of methanol and methylene chloride (Caledon Laboratories, distilled-in-glass grade or equivalent). The methylene chloride saturated material is returned to the tube furnace which has been set to 50°C and dry nitrogen purge re-established. Over a period of approximately 25 minutes the furnace temperature is increased in a step-wise manner to 180°C. The effluent gases from this operation must be vented to a fume hood. The silica is then activated for an additional period of 90 minutes at 180°C. Dried adsorbent is cooled and placed in an appropriately sized glass bottle. Sufficient concentrated sulfuric acid is added directly to the silica to yield an acid concentration of 44% based upon total weight. The material is manually shaken until no clumping can be observed, and is then transferred to a glass bottle and stored in a desiccator over phosphorus pentoxide until used. THIS REAGENT RETAINS ALL OF THE PROPERTIES OF CONCENTRATED SULFURIC ACID, AND SHOULD BE HANDLED ACCORDINGLY.

II. 10% $AgNO_3$ on Silica. The silica support for this reagent is 100/200 mesh Bio-Sil A, solvent rinsed and activated by the procedure described for 44% sulfuric acid on silica. Activated silica is placed in an appropriately sized glass bottle and its weight determined. Using the support weight, the amount of silver nitrate necessary to yield 10% by weight based on the resulting total weight is calculated. Similarly, a second calculation is made to determine the amount of de-ionized water necessary to yield 30% by weight based upon the total of silica and water only. In accordance with the determined quantities, the silver nitrate is dissolved in de-ionized water. This solution is then added to the activated silica in a stepwise fashion with shaking to produce a uniformity coated, free-flowing powder. The material is then allowed to stand for a minimum period of 30 minutes, after which it is placed in a glass tube furnace set at 70°C under a continous dry nitrogen purge. In a stepwise manner over a period of about 5 hours the temperature of the furnace is increased to 120°C. Provisions should be made to permit condensate to drain from the exit port during this phase of the preparation. From the point that condensation ceases, the adsorption is activated for an additional period of 15 hours at 125°C. The finished product is stored in an amber glass bottle in a desiccator over phosphorus pentoxide until used.

III. Basic Alumina. Chromatographic grade aluminum oxide as 100/200 mesh Bio-Rad Basic Alumina AG-10 is initially dried in a glass tube furnace for 60 minutes at 300°C under a continuous dry nitrogen purge. It is then removed from the furnace, cooled to ambient temperature, and rinsed with 150 ml of methylene chloride. The methylene chloride saturated material is returned to the tube furnace (again set at 50°C) and the dry nitrogen purge re-established, over a period of 25 minutes the furnace temperature is increased to 180°C and this temperature is maintained until solvent condensation at the exit-port ceases. Effluent gases must be vented to a fume hood. The basic alumina is then activated for an additional period of 90 minutes at 300°C. Activated adsorbent is stored in a glass bottle in a desiccator over phosphorus pentoxide until used.

IV. Silica. This reagent is prepared from chromatographic grade silicic acid purified and activated as described for the preparation of 44% sulfuric acid on silica (1).

V. 33% IM NaOH on Silica. This silica support for this reagent is 100/200-mesh Bio-Sil A, solvent rinsed and activated by the procedure described previously. Activated silica is weighed into appropriately sized glass bottle. Based upon this support weight, the amount of IM aqueous sodium hydroxide necessary to yield a reagent containing 33% by weight is added in a stepwise fashion with shaking to produce a uniformly coated, free-flowing powder. This material is stored in a glass bottle until used. Do not store in a desiccator.

Chemicals and Solvents. All solvents are Caledon distilled-in-glass grade, and are tested by submitting them to the analytical procedure in order to verify the absence of contamination. Laboratory chemicals (H_2SO_4, NaOH, $AgNO_3$) are ACS reagent-grade (J. T. Baker) and are also checked for background contamination.

PROCEDURE

Sample preparation for incinerator samples involves three basic steps: (1) chlorinated dioxins removal via a hydrocarbon extraction, (2) chemically modified adsorbent treatment of extract to effect bulk matrix removal of oxidizables, (3) chemically-modified reagent and adsorbent treatment to remove bulk common chemical interferences.

Bulk matrix removal is accomplished by passing the residue extract solution through a chromatographic column prepared as follows. The column is thoroughly washed and dried just prior to use via the same procedure described for the Soxhlet extractor. A glass wool plug is inserted into the end of the column to serve as a bed support and the following reagents are then carefully weighed directly into the column: 1.0 g silica (bottom layer), 2.0 g 33% 1 M sodium hydroxide on silica, 1.0 g silica, 4.0 g 44% concentrated sulfuric acid on silica, and 2.0 g silica (top layer). the freshly packed column is then immediately prewashed with 60 mL hexane and the effluent discarded. The residue extract is then passed through the column followed by 3 x 5 mL hexane rinses of the sample container. The column is permitted to drain to bed level between consecutive addition, and following these rinses an additional 30 mL of hexane is passed through the system to ensure complete removal of chlorinated dioxins. Throughout this process the top of the column is covered with an inverted beaker to prevent introduction of extraneous particulate matter. The entire effluent is collected in a 150 mL round bottom flask which is then evaporated to 5 mLs rotary. The packing is retained for chlorophenol analysis. Because we have observed low recoveries for lower chlorinated dioxins (TCDD's) when benzene solutions containing little or no other non-volatile residues were evaporated by this procedure, a single drop (approximately 25 mg of iso-octane is added to the reagent blank residue prior to its evaporation. Although rarely required, this technique may also be applied to sample residues which appear to be extremely clean.

The second clean-up consists of a dual column system. The top column is packed with a 1.5 g 10% silver nitrate on silica. The bottom column is packed with 5.0 g basic alumina. The top column is fitted directly into the reservoir of the bottom column. The sample residue is transferred onto the top column and the round bottom rinsed with 3 x 5 mLs of hexane. When the hexane is 2 to 3 mLs from the top of the packing, 100 mLs of hexane is added to the top column using a 100 mLs capacity reservoir. The reservoir is covered with an inverted beaker to prevent introduction of extraneous particulates. When completely dry the effluent end of the top column is rinsed into the bottom column using several mL of hexane. the top column is now discarded. A new reservoir is placed onto the bottom column and the following solvents are eluted through the column. 20 mLs 10% CCl_4/hexane, 20 mLs hexane and 40 mLs methylene chloride. The 40 mLs of methylene chloride collected in a pre-cleaned centrifuge tube is retained for further analysis of PCDD, PCDF. The 10% CCl_4/hexane and 20 mLs hexane fractions are combined and analyzed for chlorobenzenes. Extreme care is taken when handling the methylene chloride fraction, it contains all TCDD, P_5CDD, H_6CDD, H_7CDD, OCDD and all PCDF isomers. 1 mL of isooctane is then added to the 40 mL methylene chloride fraction and it is concentrated under a stream of ultra-pure nitrogen to 1 mL. This 1 mL is then quantitatively transferred to a Reacti-vial and the resulting extract is concentrated down to micro-litre volumes using ultra-pure nitrogen.

APPENDIX II

SWARU ANALYTICAL DATA

1. Florisil, Impinger, Filter Blanks for PCDDs/PCDFs
2. Feed Samples: PCDDs/PCDFs
3. Combined (Bottom) Ash Samples: PCDDs/PCDFs
4. Precipitator Flyash Samples: PCDDs/PCDFs
5. Test 1 to 15: Train Analyses for PCDDs/PCDFs
6. Process Samples: PCBs, Chlorophenols, Chlorobenzenes
7. Stack Samples: PCBs, Chlorophenols, Chlorobenzenes

TABLE 1

SWARU INCINERATOR: Analysis of Florisil Blanks for PCDDs/PCDFs in Nanograms per Sample,
Corrected for Spike Recoveries

CONGENER	1	4	5	6	7	8	9	10	11	12	13	14	15
$\mathrm{T_4CDD}$	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.4	ND	ND	ND
$\mathrm{T_4CDF}$	ND	ND	ND	0.2	ND	ND	0.6	ND	ND	2.8	1.0	0.8	0.5
$\mathrm{P_5CDD}$	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.1	ND	ND	ND
$\mathrm{P_5CDF}$	ND	ND	ND	0.3	ND	ND	ND	ND	ND	4.2	1.9	1.0	0.1
$\mathrm{H_6CDD}$	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.9	0.3	ND	ND
$\mathrm{H_6CDF}$	ND	ND	ND	0.1	ND	ND	ND	ND	ND	2.1	0.7	0.5	ND
$\mathrm{H_7CDD}$	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.1	ND	ND	ND
$\mathrm{H_7CDF}$	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
OCDD	ND	ND	ND	0.1	ND	ND	ND	ND	ND	0.1	ND	ND	ND
OCDF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total*	ND	ND	ND	0.7	ND	ND	0.6	ND	ND	12	3.9	2.3	0.6
Spike Recoveries(%)													
^{13}C-2,3,7,8-TCDD	43	40	8	39	7	43	63	85	45	100	84	37	80
^{13}C-OCDD	12	25	42	70	36	11	24	6	50	335	400	26	198

* Totals were rounded off to two significant digits

TABLE 1 (Continued)

SWARU INCINERATOR: Analysis of Impinger Blanks for PCDDs/PCDFs in Nanograms per Sample, Corrected for Spike Recoveries

CONGENER	1	4	5	6	7	8	9	10	11	12	13	14	15
T_4CDD	ND	ND	ND	ND	ND	13	1.2	ND	ND	ND	ND	ND	6.1
T_4CDF	3.5	ND	ND	ND	ND	85	2.8	2.0	ND	1.8	ND	ND	11
P_5CDD	ND	ND	ND	ND	ND	16	ND	ND	ND	ND	ND	ND	6.8
P_5CDF	ND	ND	ND	ND	ND	53	1.5	ND	ND	3.0	3.3	0.2	15
H_6CDD	ND	ND	ND	ND	ND	7.0	ND	ND	ND	ND	ND	ND	24
H_6CDF	ND	ND	ND	ND	ND	19	ND	ND	ND	ND	ND	ND	6.4
H_7CDD	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.9
H_7CDF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
OCDD	ND	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.7
OCDF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total*	3.5	0.1	ND	ND	ND	190	5.5	2.0	ND	4.8	3.3	0.2	75
Spike Recoveries(%)													
^{13}C-2,3,7,8-TCDD	6.6	120	20	67	180	64	55	120	96	160	8	33	110
^{13}C-OCDD	17	176	59	61	68	140	75	188	112	239	125	34	166

* Totals were rounded off to two significant digits

TABLE I (Continued)

SWARU INCINERATOR: Analysis of Filter Blanks for PCDDs/PCDFs in Nanograms per Sample, Corrected for Spike Recoveries

CONGENER	1	4	5	6	7	8	9	10	11	12	13	14	15
T_4CDD	2.8	0.5	ND	0.5	0.2	1.0	1.5	0.1	ND	ND	0.2	0.1	6.4
T_4CDF	7.2	0.6	ND	1.3	0.4	2.7	13	1.0	ND	ND	0.3	0.6	9.7
P_5CDD	2.8	0.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	8.2
P_5CDF	6.4	0.6	ND	ND	ND	ND	ND	0.4	ND	ND	0.5	0.4	8.8
H_6CDD	0.7	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	14
H_6CDF	0.7	0.1	ND	ND	ND	ND	ND	0.2	ND	ND	ND	ND	13
H_7CDD	1.6	0.2	ND	ND	ND	ND	2.9	ND	ND	ND	ND	ND	6.9
H_7CDF	1.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.4
OCDD	0.9	0.2	ND	ND	ND	ND	1.4	0.2	ND	ND	ND	ND	5.9
OCDF	ND	trace	ND	ND	ND	ND	0.6	ND	ND	ND	ND	ND	0.7
Total*	25	2.5	ND	1.8	0.6	3.7	19	1.9	ND	ND	1.0	1.1	74
Spike Recoveries(%)													
^{13}C-2,3,7,8-TCDD	48	18	26	76	42	26	40	62	13	18	59	0.5	43
^{13}C-OCDD	36	41	50	86	27	9	125	200	34	9	52	1	68

* Totals were rounded off to two significant digits

TABLE 2

SWARU INCINERATOR: Concentrations of PCDDs/PCDFs in ng/g in Refuse, Corrected for Spike Recoveries*

	Test 1	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10	Test 11	Test 12	Test 13	Test 14	Test 15
T$_4$CDD	$0.5^{(1)}$	$2^{(2)}$	ND	$0.1^{(2)}$	ND	ND	ND	ND	ND	ND	ND	ND	ND
T$_4$CDF	ND	ND	3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P$_5$CDD	ND	$1^{(1)}$	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P$_5$CDF	ND	ND	$1^{(10)}$	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
H$_6$CDD	ND	ND	ND	ND	$1.1^{(1)}$	$0.1^{(1)}$	$0.7^{(1)}$	ND	ND	ND	ND	$1.1^{(3)}$	$0.1^{(1)}$
H$_6$CDF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
H$_7$CDD	$0.3^{(2)}$	$0.3^{(2)}$	$2^{(2)}$	$0.6^{(2)}$	$1.3^{(2)}$	$0.6^{(2)}$	$1.0^{(2)}$	$1.3^{(2)}$	$1.8^{(2)}$	$1.7^{(2)}$	$20^{(2)}$	$3.5^{(2)}$	$0.7^{(2)}$
H$_7$CDF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	$0.3^{(1)}$	ND
OCDD	8	7	2	3	11	5.8	10	16	14	7.9	77	25	29
OCDF	25	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.3	0.1	ND
Total**	34	10	8.0	3.7	13	6.5	12	17	16	9.6	97	30	30
Spike Recoveries(%)													
^{13}C-2,3,7,8-TCDD	4	10	29	30	28	22	25	16	22	7	1	14	12
^{13}C-OCDD	11	11	34	55	56	33	45	8	16	7	3	14	10

* Numbers in brackets denote the number of isomers detected.

** Totals were rounded off to two significant digits

TABLE 3

SWARU INCINERATOR: Concentrations of PCDDs/PCDFs in ng/g in Combined Ash, Corrected for Spike Recoveries*

Test No.	1	4	5	6	7	8	9	10	11	12	13	14	15
T$_4$CDD	0.1$^{(10)}$	ND	ND	-	ND	0.7$^{(5)}$	ND	0.1$^{(4)}$	0.1$^{(4)}$	0.2$^{(2)}$	0.1$^{(5)}$	0.4$^{(12)}$	0.1$^{(5)}$
T$_4$CDF	0.1$^{(4)}$	ND	ND	-	0.3$^{(13)}$	ND	ND	ND	ND	ND	ND	0.8$^{(14)}$	ND
P$_5$CDD	ND	ND	ND	-	ND	ND	ND	ND	ND	ND	ND	0.9$^{(12)}$	ND
P$_5$CDF	0.5$^{(9)}$	ND	ND	-	0.6$^{(9)}$	ND	0.1$^{(8)}$	ND	ND	ND	ND	1.5$^{(14)}$	ND
H$_6$CDD	0.2$^{(5)}$	ND	ND	-	ND	ND	0.1$^{(6)}$	ND	ND	ND	ND	1.2$^{(7)}$	ND
H$_6$CDF	0.5$^{(7)}$	ND	ND	-	0.4$^{(4)}$	ND	0.2$^{(8)}$	ND	ND	ND	ND	1.1$^{(9)}$	ND
H$_7$CDD	0.1$^{(1)}$	ND	ND	-	ND	ND	0.1$^{(2)}$	ND	ND	ND	ND	0.5$^{(2)}$	0.1$^{(2)}$
H$_7$CDF	ND	ND	ND	-	ND	ND	0.1$^{(3)}$	ND	ND	ND	ND	0.5$^{(4)}$	ND
OCDD	0.2	ND	ND	-	ND	ND	0.2	ND	ND	0.3	ND	0.3	0.2
OCDF	ND	ND	ND	-	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total**	1.7	ND	ND	-	1.3	0.7	0.8	0.1	0.1	0.5	0.1	7.2	0.4
Spike Recoveries(%)													
^{13}C-2,3,7,8-TCDD	45	330	39	-	16	130	270	75	72	260	130	72	98
^{13}C-OCDD	43	26	76	-	65	220	116	13	51	103	71	9	48

- Sample for Test 6 was lost in preparation.

* Numbers in brackets denote the number of isomers detected.

** Totals were rounded off to two significant digits

TABLE 4

SWARU INCINERATOR: Concentration of PCDDs/PCDFs in ng/g in Flyash, Corrected for Spike Recoveries*

Congener	Test 1	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10	Test 11	Test 12	Test 13	Test 14	Test 15
T$_4$CDD	7.9$^{(13)}$	12$^{(13)}$	2.6$^{(13)}$	2.9$^{(13)}$	2.6$^{(13)}$	2.7$^{(12)}$	1.6$^{(9)}$	2.3$^{(12)}$	1.8$^{(12)}$	2.5$^{(12)}$	2.3$^{(12)}$	4.6$^{(12)}$	1.7$^{(12)}$
T$_4$CDF	36$^{(15)}$	19$^{(14)}$	8.7$^{(15)}$	12$^{(14)}$	10$^{(14)}$	14$^{(13)}$	9.1$^{(12)}$	5.1$^{(15)}$	9.4$^{(13)}$	4.5$^{(14)}$	9.3$^{(13)}$	8.1$^{(15)}$	8.8$^{(12)}$
P$_5$CDD	9.0$^{(12)}$	25$^{(12)}$	6.1$^{(12)}$	3.1$^{(12)}$	4.5$^{(11)}$	3.7$^{(11)}$	2.8$^{(12)}$	5.2$^{(12)}$	3.4$^{(12)}$	5.2$^{(11)}$	3.8$^{(11)}$	9.7$^{(12)}$	2.0$^{(11)}$
P$_5$CDF	30$^{(11)}$	40$^{(12)}$	19$^{(12)}$	13$^{(10)}$	19$^{(10)}$	22$^{(10)}$	8.3$^{(10)}$	11$^{(13)}$	15$^{(12)}$	8.5$^{(12)}$	13$^{(10)}$	15$^{(13)}$	9.5$^{(10)}$
H$_6$CDD	8.5$^{(7)}$	42$^{(7)}$	21$^{(7)}$	3.2$^{(7)}$	4.2$^{(7)}$	2.7$^{(6)}$	2.4$^{(6)}$	6.7$^{(7)}$	3.6$^{(7)}$	6.4$^{(7)}$	3.3$^{(7)}$	13$^{(7)}$	1.5$^{(7)}$
H$_6$CDF	15$^{(10)}$	35$^{(9)}$	40$^{(8)}$	4.6$^{(8)}$	22$^{(10)}$	12$^{(9)}$	5.6$^{(5)}$	10$^{(8)}$	10$^{(8)}$	7.2$^{(9)}$	8.5$^{(9)}$	12$^{(9)}$	3.9$^{(8)}$
H$_7$CDD	4.7$^{(2)}$	9.2$^{(2)}$	1.7$^{(2)}$	1.1$^{(2)}$	1.3$^{(2)}$	0.2$^{(2)}$	0.7$^{(2)}$	2.0$^{(2)}$	0.6$^{(2)}$	1.8$^{(2)}$	1.0$^{(2)}$	4.9$^{(2)}$	0.5$^{(2)}$
H$_7$CDF	7.4$^{(4)}$	9.2$^{(4)}$	2.1$^{(4)}$	1.2$^{(4)}$	2.3$^{(4)}$	0.8$^{(3)}$	0.8$^{(1)}$	2.3$^{(3)}$	1.3$^{(4)}$	1.6$^{(4)}$	1.8$^{(4)}$	5.3$^{(4)}$	0.9$^{(3)}$
OCDD	2.4	6.0	1.9	0.9	1.8	0.2	0.2	1.1	0.2	1.0	0.4	3.1	0.5
OCDF	0.3	2.1	0.1	ND	0.6	ND	ND	0.1	ND	0.1	ND	0.2	ND
Total**	120	200	100	42	68	58	32	46	45	39	43	76	29
Spike Recoveries(%)													
^{13}C-2,3,7,8-TCDD	190	170	150	260	330	51	86	97	98	130	120	72	59
^{13}C-OCDD	130	390	1000	330	590	120	60	150	160	150	130	77	42

* Numbers in brackets denote the number of isomers detected.

** Totals were rounded off to two significant digits

TABLE 5

SWARU TEST NO. 1: PCDD/PCDF in Train Samples* in Nanograms, Corrected for Spike Recoveries

Congener	Filter		Impinger	Florisil #1	Florisil #2	Total**
	1st 16 hr	2nd 16 hr				
T$_4$CDD	400$^{(13)}$	3$^{(13)}$	630$^{(13)}$	67$^{(13)}$	6$^{(13)}$	1100
T$_4$CDF	2500$^{(15)}$	15$^{(15)}$	3800$^{(15)}$	400$^{(14)}$	38$^{(15)}$	6800
P$_5$CDD	510$^{(12)}$	12$^{(12)}$	600$^{(12)}$	64$^{(12)}$	6$^{(12)}$	1200
P$_5$CDF	2400$^{(14)}$	19$^{(10)}$	2800$^{(12)}$	440$^{(14)}$	17$^{(12)}$	5700
H$_6$CDD	540$^{(6)}$	6$^{(6)}$	310$^{(6)}$	44$^{(6)}$	4$^{(6)}$	900
H$_6$CDF	1300$^{(6)}$	7$^{(4)}$	790$^{(5)}$	130$^{(6)}$	10$^{(6)}$	2200
H$_7$CDD	850$^{(2)}$	4$^{(1)}$	71$^{(2)}$	29$^{(2)}$	2$^{(1)}$	960
H$_7$CDF	1400$^{(2)}$	1$^{(1)}$	210$^{(3)}$	83$^{(4)}$	0.8$^{(1)}$	1700
OCDD	450	17	17	8	0.2	490
OCDF	220	2	93	4	0.1	320
Total**	11000	86	9300	1300	84	22000
Spike Recoveries(%)						
^{13}C-2,3,7,8-TCDD	35	ND	72	45	52	
^{13}C-OCDD	19	ND	72	24	21	

* Numbers in brackets denote the number of isomers observed.

** Totals were rounded off to two significant digits

TABLE 5 (Continued)

SWARU TEST NO. 4: PCDD/PCDF in Train Samples* in Nanograms, Corrected for Spike Recoveries

Congener	Filter		Impinger	Florisil #1	Florisil #2	Total**
	1st 16 hr	2nd 16 hr				
$\mathrm{T_4CDD}$	$42^{(12)}$	ND	$450^{(12)}$	$86^{(12)}$	$5^{(12)}$	580
$\mathrm{T_4CDF}$	$170^{(14)}$	ND	$1300^{(14)}$	$240^{(15)}$	$14^{(14)}$	1700
$\mathrm{P_5CDD}$	$140^{(10)}$	ND	$610^{(12)}$	$74^{(11)}$	$5^{(11)}$	830
$\mathrm{P_5CDF}$	$290^{(9)}$	$0.4^{(7)}$	$1400^{(10)}$	$160^{(11)}$	$11^{(11)}$	1900
$\mathrm{H_6CDD}$	$220^{(6)}$	ND	$790^{(6)}$	$58^{(5)}$	$4^{(6)}$	1100
$\mathrm{H_6CDF}$	$240^{(5)}$	ND	$870^{(5)}$	$54^{(5)}$	$4^{(6)}$	1200
$\mathrm{H_7CDD}$	$130^{(1)}$	$0.1^{(1)}$	$200^{(1)}$	$110^{(1)}$	$0.3^{(1)}$	440
$\mathrm{H_7CDF}$	$22^{(1)}$	ND	$39^{(1)}$	$27^{(1)}$	$0.5^{(1)}$	89
OCDD	240	0.2	270	27	1.1	540
OCDF	40	ND	32	18	0.3	90
Total**	1500	0.7	6000	850	45	8400
Spike Recoveries(%)						
^{13}C-2,3,7,8-TCDD	53	ND	74	80	86	
^{13}C-OCDD	50	ND	59	11	37	

* Numbers in brackets denote the number of isomers observed.

** Totals were rounded off to two significant digits

TABLE 5 (Continued)

SWARU TEST NO. 5: PCDD/PCDF in Train Samples* in Nanograms, Corrected for Spike Recoveries

Congener	Filter		Impinger	Florisil #1	Florisil #2	Total**
	1st 16 hr	2nd 16 hr				
T_4CDD	$250^{(13)}$	$7.3^{(12)}$	$1000^{(13)}$	$130^{(12)}$	$12^{(12)}$	1400
T_4CDF	$1500^{(15)}$	$35^{(15)}$	$5500^{(14)}$	$800^{(14)}$	$65^{(14)}$	7900
P_5CDD	$320^{(12)}$	$14^{(12)}$	$1200^{(10)}$	$100^{(10)}$	$6.8^{(10)}$	1600
P_5CDF	$1500^{(10)}$	$52^{(10)}$	$5500^{(7)}$	$300^{(9)}$	$18^{(7)}$	7400
H_6CDD	$520^{(6)}$	$14^{(7)}$	$1200^{(3)}$	$48^{(5)}$	$2.0^{(3)}$	1800
H_6CDF	$1100^{(5)}$	$25^{(8)}$	$2200^{(3)}$	$92^{(3)}$	$3.2^{(3)}$	3400
H_7CDD	$450^{(2)}$	$4.5^{(1)}$	$310^{(1)}$	$17^{(1)}$	$2.1^{(1)}$	780
H_7CDF	$780^{(4)}$	$1.0^{(1)}$	$610^{(1)}$	$2.9^{(1)}$	ND	1400
OCDD	670	4.4	170	17	ND	860
OCDF	55	0.9	59	2.9	ND	120
Total**	7100	160	18000	1500	110	27000
Spike Recoveries(%)						
^{13}C-2,3,7,8-TCDD	110	0.5	31	25	34	
^{13}C-OCDD	94	1.1	16	35	14	

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* Numbers in brackets denote the number of isomers observed.

** Totals were rounded off to two significant digits

TABLE 5 (Continued)

SWARU TEST NO. 6: PCDD/PCDF in Train Samples* in Nanograms, Corrected for Spike Recoveries

Congener	Filter		Impinger	Florisil #1	Florisil #2	Total**
	1st 16 hr	2nd 16 hr				
T_4CDD	3600$^{(12)}$	52$^{(11)}$	500$^{(11)}$	52$^{(11)}$	4.4$^{(12)}$	4200
T_4CDF	8800$^{(16)}$	130$^{(15)}$	1100$^{(14)}$	110$^{(14)}$	11$^{(15)}$	10000
P_5CDD	2700$^{(12)}$	55$^{(12)}$	140$^{(12)}$	22$^{(12)}$	2.2$^{(11)}$	2900
P_5CDF	7600$^{(13)}$	35$^{(12)}$	460$^{(12)}$	46$^{(12)}$	4.4$^{(12)}$	8100
H_6CDD	1700$^{(7)}$	34$^{(7)}$	64$^{(7)}$	4$^{(7)}$	0.2$^{(7)}$	1800
H_6CDF	2300$^{(9)}$	80$^{(8)}$	96$^{(7)}$	8$^{(8)}$	0.2$^{(8)}$	2500
H_7CDD	300$^{(1)}$	7.1$^{(1)}$	8$^{(1)}$	0.8$^{(1)}$	ND	320
H_7CDF	56$^{(1)}$	1.3$^{(1)}$	ND	ND	ND	57
OCDD	310	7.2	3.2	0.3	0.1	320
OCDF	59	0.9	ND	0.3	ND	60
Total**	27000	400	2400	240	23	30000
Recoveries(%)						
^{13}C-T_4CDD	17	ND	76	50	45	
^{13}C-OCDD	27	0.1 ng	25	39	71	

* Numbers in brackets denote the number of isomers observed.

** Totals were rounded off to two significant digits

TABLE 5 (Continued)

SWARU TEST NO. 7: PCDD/PCDF in Train Samples* in Nanograms, Corrected for Spike Recoveries

Congener	Filter		Impinger	Florisil #1	Florisil #2	Total**
	1st 16 hr	2nd 16 hr				
T_4CDD	$460^{(11)}$	$3.0^{(12)}$	$350^{(12)}$	$56^{(12)}$	$5.2^{(12)}$	870
T_4CDF	$2100^{(15)}$	$8.4^{(14)}$	$1800^{(14)}$	$260^{(14)}$	$19^{(12)}$	4200
P_5CDD	$1000^{(11)}$	$5.3^{(12)}$	$350^{(11)}$	$42^{(11)}$	$7.0^{(8)}$	1400
P_5CDF	$3900^{(10)}$	$14^{(12)}$	$3100^{(8)}$	$110^{(8)}$	$13^{(6)}$	7100
H_6CDD	$1200^{(6)}$	$11^{(7)}$	$640^{(4)}$	$21^{(5)}$	ND	1900
H_6CDF	$2200^{(6)}$	$13^{(9)}$	$1600^{(3)}$	$27^{(4)}$	$7.6^{(2)}$	3800
H_7CDD	$670^{(1)}$	$4.2^{(1)}$	$48^{(1)}$	$16^{(1)}$	$1.4^{(1)}$	740
H_7CDF	$160^{(1)}$	$0.5^{(1)}$	$7.2^{(1)}$	$3.0^{(1)}$	ND	170
OCDD	310	6.9	11	2.8	0.7	330
OCDF	120	0.9	7.2	1.5	0.3	130
Total**	12000	67	7900	540	54	21000
Spike Recoveries(%)						
^{13}C-2,3,7,8-TCDD	57	ND	110	52	33	
^{13}C-OCDD	52	0.06 ng	83	40	68	

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* Numbers in brackets denote the number of isomers observed.

** Totals were rounded off to two significant digits

TABLE 5 (Continued)

SWARU TEST NO. 8: PCDD/PCDF in Train Samples* in Nanograms, Corrected for Spike Recoveries

Congener	Filter		Impinger	Florisil #1	Florisil #2	Total**
	1st 16 hr	2nd 16 hr				
T$_4$CDD	$160^{(12)}$	$0.6^{(11)}$	$400^{(12)}$	$120^{(12)}$	$7.7^{(12)}$	690
T$_4$CDF	$710^{(14)}$	$3.5^{(12)}$	$1700^{(15)}$	$760^{(15)}$	$48^{(15)}$	3200
P$_5$CDD	$220^{(12)}$	$1.0^{(12)}$	$170^{(10)}$	$100^{(10)}$	$5.4^{(15)}$	500
P$_5$CDF	$970^{(10)}$	$4.8^{(10)}$	$860^{(9)}$	$450^{(9)}$	$25^{(11)}$	2300
H$_6$CDD	$320^{(7)}$	$0.9^{(7)}$	$170^{(4)}$	$49^{(4)}$	$2.7^{(6)}$	540
H$_6$CDF	$570^{(9)}$	$2.8^{(6)}$	$330^{(3)}$	$130^{(2)}$	$4.4^{(5)}$	1000
H$_7$CDD	$190^{(1)}$	$0.1^{(1)}$	$54^{(1)}$	$53^{(1)}$	$1.3^{(1)}$	300
H$_7$CDF	$53^{(1)}$	ND	$13^{(1)}$	$1.4^{(1)}$	$0.2^{(1)}$	68
OCDD	140	ND	30	2.8	0.4	170
OCDF	28	ND	9.3	0.5	ND	38
Total	3400	14	3700	1700	95	8900
Spike Recoveries(%)						
^{13}C-2,3,7,8-TCDD	95	ND	63	55	108	
^{13}C-OCDD	36	ND	150	43	120	

* Numbers in brackets denote the number of isomers observed.

** Totals were rounded off to two significant digits

TABLE 5 (Continued)

SWARU TEST NO. 9: PCDD/PCDF in Train Samples* in Nanograms, Corrected for Spike Recoveries

Congener	Filter		Impinger	Florisil #1	Florisil #2	Total**
	1st 16 hr	2nd 16 hr				
T$_4$CDD	$900^{(11)}$	$1.4^{(12)}$	$90^{(12)}$	$27^{(12)}$	ND	1000
T$_4$CDF	$4600^{(16)}$	$7.3^{(12)}$	$710^{(13)}$	$220^{(13)}$	ND	5500
P$_5$CDD	$680^{(11)}$	$1.0^{(12)}$	$72^{(10)}$	$10^{(11)}$	ND	760
P$_5$CDF	$2900^{(11)}$	$4.9^{(8)}$	$420^{(8)}$	$36^{(8)}$	ND	3400
H$_6$CDD	$850^{(7)}$	$0.4^{(4)}$	$22^{(6)}$	$4.1^{(4)}$	ND	880
H$_6$CDF	$1800^{(10)}$	$1.5^{(4)}$	$81^{(3)}$	$14^{(6)}$	ND	1900
H$_7$CDD	$230^{(1)}$	$0.04^{(1)}$	$3.1^{(1)}$	$1.3^{(1)}$	ND	230
H$_7$CDF	$59^{(1)}$	ND	$0.7^{(1)}$	ND	ND	60
OCDD	220	ND	1.9	ND	ND	220
OCDF	32	ND	0.7	ND	ND	33
Total**	12000	17	1400	310	ND	14000
Spike Recoveries(%)						
^{13}C-2,3,7,8-TCDD	41	0.1	96	44	25	
^{13}C-OCDD	37	ND	85	8	7	

* Numbers in brackets denote the number of isomers observed.

** Totals were rounded off to two significant digits

TABLE 5 (Continued)

SWARU TEST NO. 10: PCDD/PCDF in Train Samples* in Nanograms, Corrected for Spike Recoveries

Congener	Filter		Impinger	Florisil #1	Florisil #2	Total**
	1st 16 hr	2nd 16 hr				
T_4CDD	$81^{(12)}$	$0.3^{(9)}$	$630^{(11)}$	$110^{(12)}$	$150^{(8)}$	970
T_4CDF	$270^{(15)}$	$1.1^{(13)}$	$2200^{(15)}$	$350^{(17)}$	$980^{(15)}$	3800
P_5CDD	$130^{(12)}$	$1.7^{(11)}$	$500^{(11)}$	$120^{(12)}$	$210^{(10)}$	960
P_5CDF	$270^{(12)}$	$2.5^{(9)}$	$870^{(9)}$	$260^{(13)}$	$270^{(6)}$	1700
H_6CDD	$250^{(7)}$	$1.9^{(7)}$	$570^{(7)}$	$81^{(7)}$	$31^{(5)}$	930
H_6CDF	$310^{(9)}$	$2.1^{(5)}$	$700^{(9)}$	$100^{(8)}$	$67^{(4)}$	1200
H_7CDD	$130^{(1)}$	$0.5^{(1)}$	$190^{(1)}$	$64^{(1)}$	$4.4^{(1)}$	390
H_7CDF	$26^{(1)}$	ND	$33^{(1)}$	$14^{(1)}$	ND	73
OCDD	130	0.3	120	39	3.2	290
OCDF	23	0.02	18	10	1.5	53
Total**	1600	10	5800	1100	1700	10000
Spike Recoveries(%)						
^{13}C-2,3,7,8-TCDD	48	ND	30	74	15	
^{13}C-OCDD	27	0.01 ng	16	12	130	

* Numbers in brackets denote the number of isomers observed.

** Totals were rounded off to two significant digits

TABLE 5 (Continued)

SWARU TEST NO. 11: PCDD/PCDF in Train Samples* in Nanograms, Corrected for Spike Recoveries

Congener	Filter		Impinger	Florisil #1	Florisil #2	Total**
	1st 16 hr	2nd 16 hr				
T_4CDD	$390^{(11)}$	$7.4^{(13)}$	$200^{(12)}$	$22^{(12)}$	$30^{(12)}$	650
T_4CDF	$2700^{(14)}$	$30^{(15)}$	$1400^{(14)}$	$150^{(13)}$	$180^{(14)}$	4500
P_5CDD	$430^{(11)}$	$24^{(11)}$	$210^{(12)}$	$10^{(12)}$	$42^{(11)}$	720
P_5CDF	$2100^{(11)}$	$130^{(11)}$	$880^{(10)}$	$18^{(12)}$	$220^{(8)}$	3300
H_6CDD	$430^{(7)}$	$48^{(7)}$	$79^{(7)}$	$110^{(9)}$	$15^{(7)}$	680
H_6CDF	$1100^{(9)}$	$220^{(8)}$	$210^{(9)}$	$7.5^{(7)}$	$42^{(8)}$	1600
H_7CDD	$310^{(1)}$	$8.5^{(2)}$	$16^{(1)}$	$31^{(1)}$	$3.8^{(1)}$	370
H_7CDF	$91^{(1)}$	$26^{(4)}$	$14^{(1)}$	$0.6^{(1)}$	ND	130
OCDD	150	2.0	6.3	ND	ND	160
OCDF	28	0.2	0.7	ND	ND	29
Total**	7700	500	3000	350	530	12000
Spike Recoveries(%)						
^{13}C-2,3,7,8-TCDD	27	ND	112	44	20	
^{13}C-OCDD	11	ND	43	20	4	

* Numbers in brackets denote the number of isomers observed.

** Totals were rounded off to two significant digits

TABLE 5 (Continued)

SWARU TEST NO. 12: PCDD/PCDF in Train Samples* in Nanograms, Corrected for Spike Recoveries

Congener	Filter		Impinger	Florisil #1	Florisil #2	Total**
	1st 16 hr	2nd 16 hr				
T_4CDD	$40^{(12)}$	$0.7^{(9)}$	$940^{(12)}$	$120^{(12)}$	$6.3^{(11)}$	1100
T_4CDF	$120^{(16)}$	$1.4^{(13)}$	$2800^{(15)}$	$380^{(16)}$	$19^{(16)}$	3300
P_5CDD	$95^{(12)}$	$0.4^{(9)}$	$980^{(12)}$	$130^{(12)}$	$11^{(12)}$	1200
P_5CDF	$230^{(13)}$	$1.4^{(9)}$	$2600^{(14)}$	$420^{(13)}$	$27^{(12)}$	3300
H_6CDD	$140^{(7)}$	$0.3^{(4)}$	$1400^{(7)}$	$92^{(7)}$	$8.4^{(7)}$	1600
H_6CDF	$170^{(9)}$	$0.5^{(4)}$	$1900^{(9)}$	$130^{(9)}$	$9.9^{(9)}$	2200
H_7CDD	$140^{(1)}$	$0.1^{(1)}$	$300^{(1)}$	$58^{(1)}$	$3.3^{(1)}$	500
H_7CDF	$30^{(1)}$	ND	$69^{(1)}$	$13^{(1)}$	$0.9^{(1)}$	110
OCDD	140	0.02	220	28	2.1	390
OCDF	34	ND	58	7.5	0.3	100
Total**	1100	4.8	11000	1400	88	14000
Spike Recoveries(%)						
^{13}C-2,3,7,8-TCDD	60	1.0 ng	55	85	111	
^{13}C-OCDD	25	0.2 ng	48	24	42	

* Numbers in brackets denote the number of isomers observed.

** Totals were rounded off to two significant digits

TABLE 5 (Continued)

SWARU TEST NO. 13: PCDD/PCDF in Train Samples* in Nanograms, Corrected for Spike Recoveries

Congener	Filter		Impinger	Florisil #1	Florisil #2	Total**
	1st 16 hr	2nd 16 hr				
T_4CDD	$500^{(11)}$	$0.03^{(2)}$	$170^{(12)}$	$62^{(12)}$	ND	730
T_4CDF	$3400^{(14)}$	$0.8^{(12)}$	$1000^{(15)}$	$440^{(15)}$	$5.0^{(13)}$	4800
P_5CDD	$440^{(11)}$	$0.3^{(6)}$	$150^{(12)}$	$57^{(12)}$	ND	650
P_5CDF	$2300^{(13)}$	$1.3^{(10)}$	$1000^{(12)}$	$380^{(13)}$	$4.0^{(10)}$	3700
H_6CDD	$490^{(7)}$	$0.3^{(10)}$	$110^{(7)}$	$40^{(7)}$	ND	640
H_6CDF	$1200^{(9)}$	$0.8^{(4)}$	$290^{(9)}$	$100^{(9)}$	$0.5^{(3)}$	1600
H_7CDD	$150^{(1)}$	ND	$8.1^{(1)}$	$2.5^{(1)}$	ND	160
H_7CDF	$50^{(1)}$	ND	$3.1^{(1)}$	$1.0^{(1)}$	ND	54
OCDD	170	ND	3.1	3.5	ND	180
OCDF	50	ND	0.4	1.1	ND	52
Total**	8800	3.5	2700	1100	9.5	13000
Recoveries(%)						
^{13}C-2,3,7,8-TCDD	41	0.02 ng	27	58	58	
^{13}C-OCDD	30	ND	26	81	24	

* Numbers in brackets denote the number of isomers observed.

** Totals were rounded off to two significant digits

TABLE 5 (Continued)

SWARU TEST NO. 14: PCDD/PCDF in Train Samples* in Nanograms, Corrected for Spike Recoveries

Congener	Filter		Impinger	Florisil #1	Florisil #2	Total**
	1st 16 hr	2nd 16 hr				
T$_4$CDD	$1200^{(11)}$	$21^{(11)}$	$2300^{(10)}$	$85^{(8)}$	$0.9^{(5)}$	3600
T$_4$CDF	$2200^{(15)}$	$23^{(13)}$	$2400^{(15)}$	$110^{(16)}$	$2.1^{(7)}$	4700
P$_5$CDD	$1100^{(12)}$	$25^{(9)}$	$1500^{(12)}$	$49^{(12)}$	ND	2700
P$_5$CDF	$2000^{(13)}$	$43^{(11)}$	$2000^{(13)}$	$72^{(12)}$	ND	4100
H$_6$CDD	$1300^{(7)}$	$26^{(5)}$	$620^{(7)}$	$38^{(7)}$	ND	2000
H$_6$CDF	$970^{(9)}$	$30^{(5)}$	$370^{(9)}$	$25^{(9)}$	ND	1400
H$_7$CDD	$270^{(1)}$	ND	$410^{(1)}$	$1.8^{(1)}$	ND	680
H$_7$CDF	$34^{(1)}$	ND	$390^{(1)}$	ND	ND	420
OCDD	350	ND	140	$1.0^{(1)}$	ND	490
OCDF	34	ND	13	ND	ND	47
Total**	9500	170	10000	380	3.0	20000
Recoveries(%)						
^{13}C-2,3,7,8-TCDD	63	ND	124	53	140	
^{13}C-OCDD	70	ND	12	44	49	

* Numbers in brackets denote the number of isomers observed.

** Totals were rounded off to two significant digits

TABLE 5 (Continued)

SWARU TEST NO. 15: PCDD/PCDF in Train Samples* in Nanograms, Corrected for Spike Recoveries

Congener	Filter		Impinger	Florisil #1	Florisil #2	Total**
	1st 16 hr	2nd 16 hr				
T_4CDD	$63^{(12)}$	ND	$710^{(12)}$	$49^{(12)}$	$2.6^{(10)}$	820
T_4CDF	$200^{(15)}$	$0.2^{(10)}$	$2500^{(15)}$	$190^{(16)}$	$11^{(15)}$	2900
P_5CDD	$110^{(12)}$	$0.6^{(11)}$	$1100^{(12)}$	$83^{(12)}$	$2.6^{(12)}$	1300
P_5CDF	$300^{(13)}$	$1.0^{(9)}$	$2800^{(12)}$	$210^{(13)}$	$7.1^{(12)}$	3300
H_6CDD	$220^{(7)}$	$1.5^{(6)}$	$1200^{(7)}$	$83^{(7)}$	$2.3^{(7)}$	1500
H_6CDF	$280^{(9)}$	$1.8^{(6)}$	$1700^{(9)}$	$100^{(9)}$	$2.6^{(7)}$	2100
H_7CDD	$240^{(1)}$	$0.6^{(1)}$	$950^{(1)}$	$44^{(1)}$	$0.29^{(1)}$	1200
H_7CDF	$61^{(1)}$	$0.04^{(1)}$	$250^{(1)}$	$11^{(1)}$	ND	320
OCDD	310	0.7	710	24	0.28	1000
OCDF	75	0.1	210	6.8	ND	290
Total**	1900	6.5	12000	800	29	15000
Recoveries(%)						
^{13}C-2,3,7,8-TCDD	59	ND	49	69	129	
^{13}C-OCDD	28	0.2 ng	20	25	79	

* Numbers in brackets denote the number of isomers observed.

** Totals were rounded off to two significant digits

TABLE 6

SWARU INCINERATOR: Nanograms of PCBs, Chlorophenols and Chlorobenzenes in Process Samples

	Feedstock			Bottom Ash			Precipitator Fly Ash		
Test	Chlorobenzenes	PCBs	Chlorophenols	Chlorobenzenes	PCBs	Chlorophenols	Chlorobenzenes	PCBs	Chlorophenols
1	330	900	12000	55	100	150	1000	200	ND
4	400	500	13000	ND	25	ND	220	170	12000
5	30	40000	6400	ND	15	150	120	140	1300
6	190	810	7600	ND	20	ND	120	20	750
7	2200	1500	15000	10	15	ND	130	45	1100
8	480	350	50	ND	10	50	220	110	800
9	500	320	8800	ND	ND	150	160	20	ND
10	210	350	11000	ND	ND	75	80	45	2600
11	460	1300	32000	ND	20	300	50	ND	850
12	480	610	18000	40	10	250	100	ND	1300
13	290	2500	37000	ND	15	500	56	50	1500
14	1200	860	100000	ND	ND	100	150	20	5000
15	1300	1900	78000	ND	20	200	310	85	1000

TABLE 7

SWARU INCINERATOR: Nanograms of PCBs, Chlorophenols, and Chlorobenzenes in Stack Samples

Test	Chlorobenzenes	PCBs	Chlorophenols
1	110000	370	85000
4	39000	160	37000
5	15000	630	140000
6	62000	180	74000
7	150000	560	94000
8	61000	170	78000
9	120000	460	190000
10	47000	210	158000
11	99000	4300	67000
12	68000	1200	190000
13	230000	2100	230000
14	55000	450	6200
15	46000	1200	150000

POOR

QUALITY

ORIGINAL